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of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.

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KOSMOS 60 RF KOSMOS 60 RF

Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

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and
best wishes
for the
new year

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Sharples Accelerators	Chemical Name
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62	TETRAETHYLTHIURAM DISULFIDE
57	ZINC DIMETHYLDITHIOCARBAMATE
67	ZINC DIETHYLDITHIOCARBAMATE
77	ZINC DIBUTYLDITHIOCARBAMATE
66	SELENIUM DIETHYLDITHIOCARBAMATE
	ETHYLAC
	MERAC

VULCANIZING AGENTS
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WAX
Sharples Wax (anti-sunchecking wax)

POLYMERIZATION CONTROLLER
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TYPE A — for stocks requiring unsurpassed solvent resistance.

TYPE FA — for extruded goods that must withstand aromatic blended fuels and permanent oil and weather-resistant putties.

TYPE PR-1 — for molded goods that must withstand aromatic blended fuels.

TYPE ST — for molded and extruded goods that must withstand aromatic blended fuels and low temperatures.

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MF — for liquid compounds to give films of good solvent and low temperature resistance.

WD-2 — For liquid compounds to give films which must be free from odor. Films also have excellent low temperature resistance.

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TP-90B — for plasticizing natural rubber, GR-S, Buna N and GR-M for extreme low temperature resistance.

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LP-2 — A liquid polymer of 100% solids which vulcanizes to a tough resilient solid without shrinkage when mixed with curing agents.

LP-3 — same as LP-2 but of a lower viscosity.

TACKIFIERS:

GALEX W-100 & W-100D — A non-oxidizing rosin for imparting tack to the Buna rubbers. Also valuable in GR-M compounds.

TECHNICAL INFORMATION AND SAMPLES ON REQUEST

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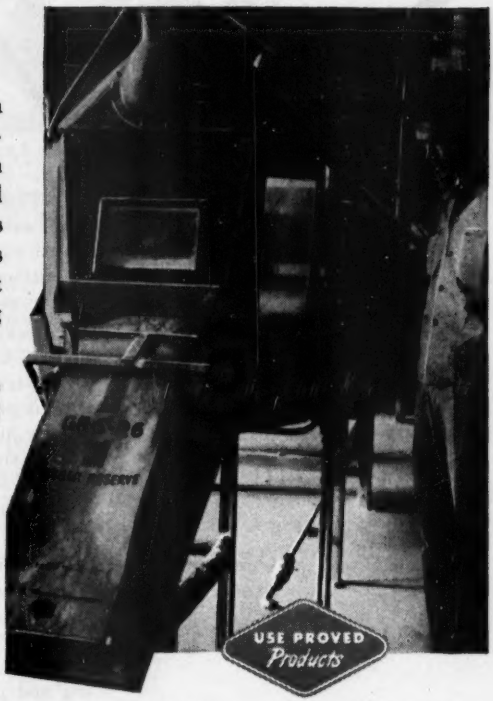
Your GR-S 26 is protected with *Wing-Stay S*

Goodyear's Top Quality, Nonstaining Antioxidant



EVERY pound of GR-S 26 on the market today is protected against oxidation with WING-STAY S—incorporated during manufacture. That's why so many compounders consider GR-S 26 the best nonstaining, non-discoloring rubber available today.

You can get equally effective protection in solid or foamed natural rubber with WING-STAY S—Goodyear's use-proved antioxidant that is in wide use in white and light-colored compounds in a range of products.

Although WING-STAY S is presently in short supply, you should investigate its potentialities *now*—and be ready to use it when normal supply returns. You can get full details and sample for your laboratory use and evaluation by writing:

Goodyear, Chemical Division
Akron 16, Ohio

GOODYEAR

Wing-Stay—T.M. The Goodyear Tire & Rubber Company, Akron, Ohio

You can get tack with Purecal in GR-S

It's a fact. Purecal* T imparts tack to GR-S – sufficient tack to hold plies together during building operations. In most cases, cementing operations can be eliminated and much of the automatic building equipment used with natural rubber can be used with GR-S.

Purecal T is easier to process in GR-S than in natural rubber. It mixes easier and faster. Because of its ultra-fine qualities, it produces tack and promotes high quality in non-black stocks. Using Purecal T, you can get excellent results at low cost in passenger tire carcasses, hose and belting products, footwear and gum stripping.

We know this—not just from laboratory tests – but mainly from work in plants. We've recorded the findings in a new booklet: "Purecal in GR-S." It contains practical information on the compounding and processing of Purecals in GR-S and cold rubber. We think you'll find it useful—we'll be glad to send it to you.

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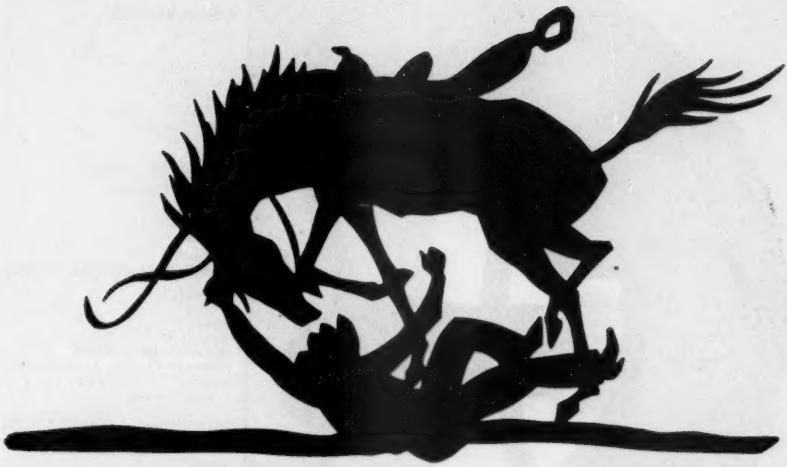

... unexpected emergency

Good riders rarely have unexpected falls, since they can fully depend upon their well-trained horses.

You as a user of carbon black can also fully depend on a continuing supply of economical-to-use **TEXAS CHANNEL BLACKS** from the Sid Richardson Carbon Co.

With the world's largest channel black plant and our own available nearby resources, we assure your present and future requirements. Let us serve you.

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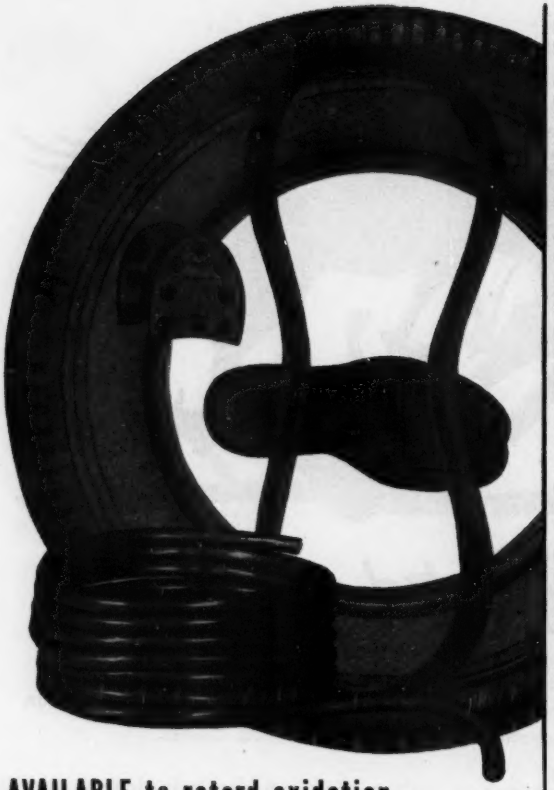
CHANNEL BLACKS

Sid Richardson
CARBON CO.
FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO



AVAILABLE to retard oxidation and flex cracking

Monsanto has *available for immediate delivery* three products with proved-in-service efficiency for retarding oxidation and flex cracking in such products as shoe soles and heels, tires, cable jackets and mechanicals. All of these antioxidants are effective in synthetic rubber, in natural rubber, in reclaimed rubber.

SANTOFLEX B — 1.0 to 2.0% of Santoflex B gives excellent results in retarding flex cracking and oxidation; 3.0 to 4.0% gives high resistance to weathering and flexing.

SANTOFLEX BX — A preferred antioxidant for retarding oxidation and flex cracking. It mildly activates accelerators of the thiazole type. Use not over 2.0% to avoid blooming.

SANTOFLEX 35 — The choice of many manufacturers for retarding oxidation and flex cracking. It mildly activates thiazole-type accelerators. Blooming can be avoided by using not over 1%.

For technical information on these and other Monsanto Chemicals for the Rubber Industry, contact MONSANTO CHEMICAL COMPANY, Rubber Service Department, 920 Brown Street, Akron 11, Ohio.

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Santoflex* B
Santoflex BX
Santoflex 35
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L

ALDEHYDE AMINE ACCELERATORS
A-32
A-77*
A-100

MERCAPTO ACCELERATORS
Santocure*
El-Sixty*
Ureka* C
Ureka Base
Mertax (Purified Thiotax)
Thiotax (2-Mercapto benzothiazole)
Thiofide* (2,2' dithio-bis benzothiazole)

GUANIDINE ACCELERATORS
Diphenyl Guanidine (D.P.G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.
R-2 Crystals
Pip-Pip
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Ethyl Thiurad (Tetra ethyl thiuram disulfide)
Mono Thiurad (Tetra methyl thiuram mono sulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

WETTING AGENTS AND DETERGENTS
Areskap* 50
Aresklene* 375
Santomerse* S
Santomerse D

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Santovar*-A
Santovar-O
Insoluble Sulfur "60"
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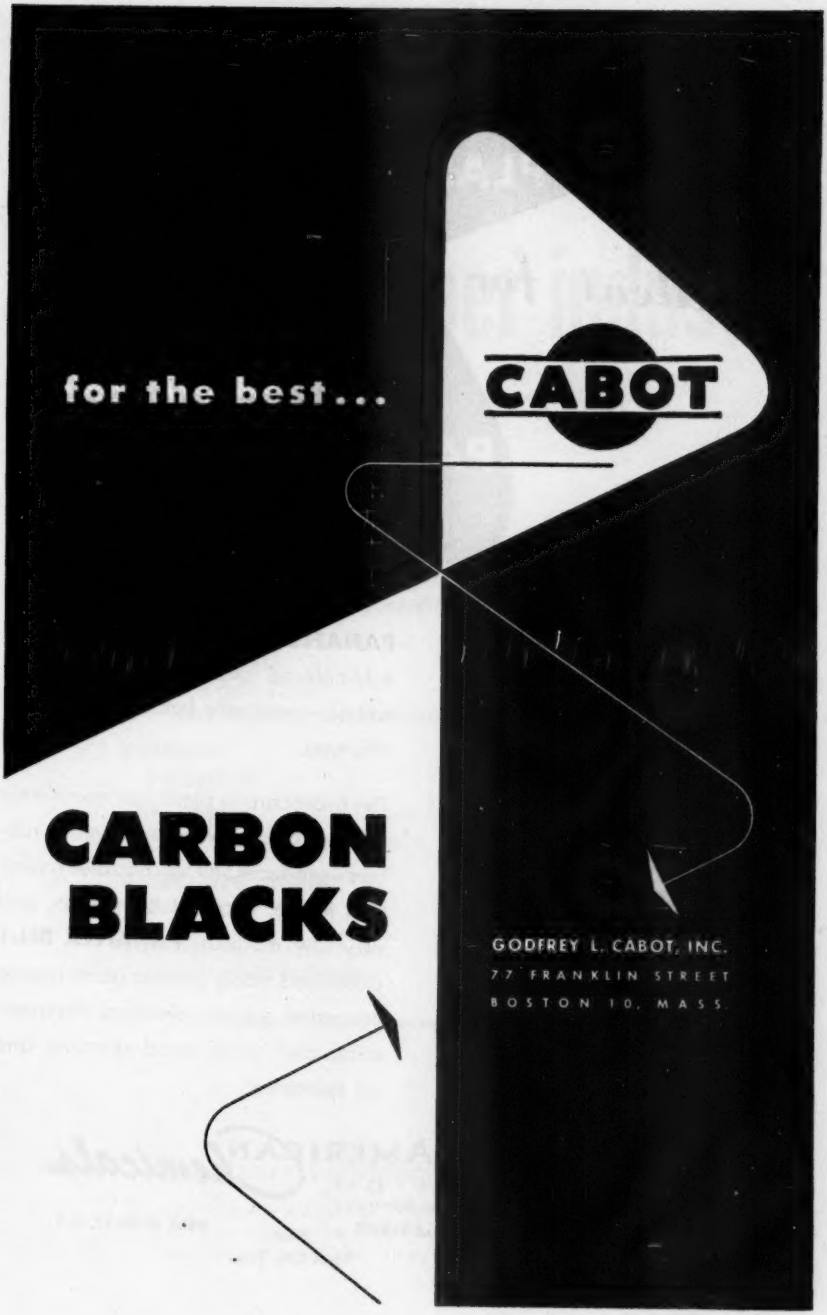
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Excellent for **LIGHT COLORED PRODUCTS**

PANAFLEX BN-1

PANAFLEX BN-1 is an economical, light-colored plasticizer for synthetic rubber — especially butadiene-acrylonitrile type.

This hydrocarbon plasticizer *completely* replaces dibutyl phthalate in nitrile rubbers—produces soft vulcanizates having high tensile, excellent elongation, and very low modulus. **PANAFLEX BN-1** plasticized stocks possess good ageing properties, superior electrical characteristics, and show good gasoline and oil resistance.

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MBTS (Benzothiazyldisulfide)
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DPG (Diphenylguanidine)
DOTG (Diorthotolylguanidine)
Accelerator 49

ANTIOXIDANT
Antioxidant 2246 *
(Non-staining, non-discoloring type)

PEPTIZER
Pepton® 22

RETARDER
Calco Retarder P.D.

STIFFENING AGENT
Calco S.A.

SULFUR
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CALCO CHEMICAL DIVISION
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You've known these familiar trademarks . . .

NOW LOOK FOR THIS TRADEMARK
to assure the same high quality in alkalies and related chemicals . . .

You can rely on the same experienced organization

Those of you who have purchased Columbia chemicals and rubber pigments from Columbia Chemical Division of Pittsburgh Plate Glass will continue to find the same competent personnel—in every department—welcoming the opportunity to serve you as Columbia-Southern . . . through strategically located plants and offices.

Production at all plants is being maintained at the highest possible levels in order to help meet the current requirements of industry. And the same district offices will continue to provide facilities that assure the most careful attention to the needs of your business.

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YOU CAN CUT THE COST OF A PASSENGER-CAR TIRE

WITH DU PONT

THIONEX-MBTS

ACCELERATION

IF YOUR PRESENT ACCELERATOR COSTS are over 35¢ per 100 pounds of GR-S, it will pay you to investigate Thionex-MBTS. Depending on the accelerator it is compared with, savings up to one-half are possible.

What's more, there is no sacrifice in processing safety or tire quality. Factory experience has proved this combination to be safe processing. Road tests show Thionex-MBTS accelerated treads deliver long mileage.

Consult Report BL-235 for complete information. Extra copies are available. Ask your district office or write, E. I. du Pont de Nemours & Co. (Inc.), Rubber Chemicals Div., Wilmington 98, Delaware.

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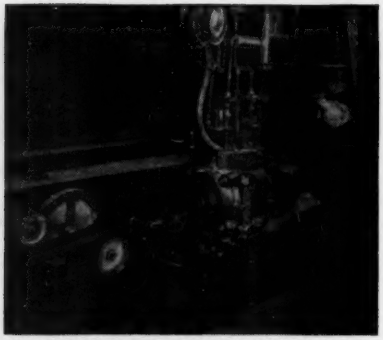
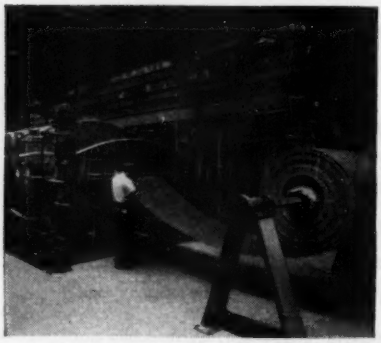
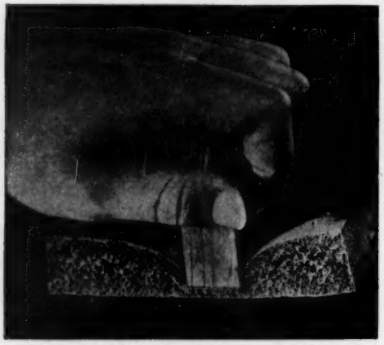
A TOY COMPANY saves $18,000 a year by using a Sun Rubber-Process Aid. Rejects due to blooming have been eliminated. Plasticization has improved so much that toys can now be molded in more intricate designs and with more eye-appeal.



A PRODUCER OF MECHANICAL RUBBER GOODS eliminated costly rejects due to scorching, by switching to a Sun Rubber-Process Aid. By properly conditioning his stock—making it easier to work—the Sun aid speeded up extruding.



AN INDUSTRIAL BELT MAKER improved the quality of his products and cut his inventory costs $6,000 a year by replacing five competitive aids with two Sun Rubber-Process Aids. Now able to buy tank-car lots, he saves still more.



A RUBBER SPONGE MAKER changed from ordinary processing oils to a Sun Rubber-Process Aid because it did not migrate, bloom, or affect his reclaim resin-type adhesives. This extra margin of safety has greatly accelerated production.

HOW 4 MANUFACTURERS HAVE BENEFITED FROM SUN'S RUBBER-PROCESS AIDS

By switching to Sun Rubber-Process Aids, each of these four manufacturers increased the efficiency of his plant, improved the quality of his products, and effected substantial savings. The results, condensed into a few words here, are typical, not unusual. For full information or the services of a Sun technical representative, call the nearest Sun Office or write to Department RC-10.

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SUN OIL COMPANY, PHILADELPHIA 3, PA. • SUN OIL COMPANY, LTD., TORONTO AND MONTREAL

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RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIV NUMBER 4

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Published under the Auspices of the
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of the
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for **RUBBER COMPOUNDING**

•

MPC (Medium Processing Channel)
STANDARD MICRONEX

•

EPC (Easy Processing Channel)
MICRONEX W-6

•

HAF (High Abrasion Furnace)
STATEX-R

•

FF (Fine Furnace)
STATEX-B

•

FEF (Fast Extruding Furnace)
STATEX-M

•

HMF (High Modulus Furnace)
STATEX-93

•

SRF (Semi-Reinforcing Furnace)
FURNEX

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Chairman....C. A. Larson (Whitney Blake Co., Hamden, Conn.). *Vice-Chairman*....G. R. Sprague (Sponge Rubber Products Co., Derby, Conn.). *Secretary*....G. A. Di Norscia (Sponge Rubber Products Co., Derby, Conn.). *Treasurer*....F. J. Rooney (General Electric Co., Bridgeport, Conn.). (Terms expire December 31, 1951.)

Detroit

Chairman....G. F. Lindner (Minnesota Mining & Manufacturing Co., Detroit). *Vice-Chairman*....G. R. Cuthbertson (U. S. Rubber Co., Detroit). *Secretary*....G. P. Hollingsworth (Minnesota Mining & Manufacturing Co., Detroit). *Treasurer*....E. V. Hindle (U. S. Rubber Co., Detroit). (Terms expire December 31, 1951.)

Los Angeles

Chairman....R. D. Abbott (R. D. Abbott Co., Los Angeles). *Associate Chairman*....R. L. Short (Kirkhill Rubber Co., Los Angeles). *Vice-Chairman*....D. C. Maddy (Harwick Standard Chemical Co., Los Angeles). *Secretary*....F. C. Johnston (Caram Manufacturing Co., Monrovia, Calif.). *Treasurer*....C. S. Hoglund (R. D. Abbott Co., Los Angeles). (Terms expire December 31, 1951.)

New York

Chairman....M. R. Buffington (Lea Fabrics, Inc., Newark, N. J.). *Vice-Chairman*....J. S. Corrigall (R. T. Vanderbilt Co., New York). *Secretary-Treasurer*....B. B. Wilson (*India Rubber World*, New York). (Terms expire December 31, 1951.)

Northern California

Chairman....J. B. Watson (Goodyear Rubber Co., San Francisco). *Vice-Chairman*....Neil McIntyre (Oliver Tire and Rubber Co., Oakland). *Secretary*....Grover Ramsey (Grove Regulator Co., Oakland). *Treasurer*....James Sanford (American Rubber Co., Oakland). (Terms expire December 31, 1951.)

Philadelphia

Chairman....H. J. Reid (Gilmer Division, U. S. Rubber Co., Philadelphia). *Vice-Chairman*....T. W. Elkin (Armstrong Cork Co., Lancaster, Pa.). *Secretary-Treasurer*....George Wyrough (R. E. Carroll Co., Trenton). (Terms expire at meeting in January 1952.)

Rhode Island

Chairman....F. V. Newman (Respro, Inc., Cranston, R. I.). *Vice-Chairman*....C. L. Kingsford (Davol Rubber Co., Providence). *Secretary-Treasurer*....R. G. Volkman (U. S. Rubber Co., Providence). (Terms expire at Fall meeting of 1951.)

SOUTHERN OHIO

Chairman....L. J. KEYES (Dayton Rubber Co., Dayton). *Vice-Chairman* ....J. E. FELDMAN (Inland Manufacturing Division, General Motors Corp., Dayton). *Secretary*....R. J. HOSKIN (Inland Manufacturing Div., General Motors Corp., Dayton). (Terms expire December 31, 1951.)

WASHINGTON, D. C.

Chairman....T. R. SCANLAN (Gates Rubber Co., Washington). *Vice-Chairman*....NORMAN BEKKEDAHL (National Bureau of Standards, Washington). *Secretary*....G. P. REINSMITH (Office of the Chief of Army Ordnance, Washington). *Treasurer*....PHILIP MITTON (Army Engineers' Research and Development Laboratories, Washington). *Recording Secretary*....ETHEL LEVINE (Navy Bureau of Ships, Washington). (Terms expire October 1952).

FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY NEW YORK, N. Y., SEPTEMBER 5–7, 1951

The 59th Meeting of the Division of Rubber Chemistry was held, in conjunction with the 75th Anniversary Meeting of the American Chemical Society in New York City, September 5–7, 1951, with headquarters at the Hotel Commodore.

The total registration of the Division of Rubber Chemistry could not be determined because of the system of joint registration of different divisions. However, the banquet, in the Ball Room of the Hotel Commodore, was attended by approximately 700 members and guests.

The Charles Goodyear award to William C. Geer was acknowledged by a lecture on the subject of "Strategy in Rubber Compounding." At the banquet, Dr. Geer was presented with the Charles Goodyear medal, certificate of honor, and honorarium. Harland Trumbull spoke of the attainments of the medallist.

The banquet was preceded by a most enjoyable cocktail party, provided by the Suppliers' Committee, headed by E. B. Curtis.

Another enjoyable feature of the meeting was the luncheon of the 25-Year Club, under the chairmanship of A. A. Somerville. This organization is growing steadily, and 175 members were present at the luncheon.

At the business meeting the Division noted with deep regret the passing of four of its members: R. M. Warner of the B. F. Goodrich Co., Akron, L. G. Whittemore of L. G. Whittemore, Inc., Boston, David G. Scott, Sr., of Scott Testers, Inc., Providence, and J. P. Maider of the Goodyear Tire & Rubber Co., Akron.

Chairman Fielding announced that the meetings in 1952 are to be in Cincinnati on April 30 and May 1–2, and in Buffalo on October 29–31. In 1953 the Division will meet with the ACS at Los Angeles in the spring and also will hold an independent meeting in Boston; in the fall of 1953 the Division will meet with the ACS in Chicago, September 9–11.

Chairman J. F. Kerscher of the Membership Committee reported more than 300 new members, making a total membership (regular and associate) of 2329. With subscribers to RUBBER CHEMISTRY & TECHNOLOGY added, the total is 2816.

J. W. Snyder of the Tellers' Committee reported that 976 votes were cast in the recent election and that, in addition to the uncontested votes for W. L.

Semon, Chairman, C. R. Haynes, Secretary, and A. W. Oakleaf, Treasurer, the balloting resulted as follows: Vice-Chairman, S. G. Byam; Director-at-Large, J. H. Ingmanson; new Directors for two years, S. M. Boyd, R. A. Claussen, H. L. Ebert, H. L. Fisher, B. S. Garvey, Jr., P. O. Powers, and G. M. Wolf.

The technical sessions comprised five symposia, which had been organized by individual chairmen, who opened the symposia with short introductory addresses and presided at the symposia.

COMPOUNDING

Chairman, A. E. Juve, B. F. Goodrich Co., Brecksville, O.

1. The Compounder in the Rubber Industry. B. S. Garvey, Jr. (Sharples Chemicals, Inc., Wayne, Pa.)
2. The Significance of Breakage of Carbon-Rubber Networks by Applied Stress. A. F. Blanchard and D. Parkinson (Dunlop Rubber Co., Birmingham, England).
3. Carbon Black Dispersion and Reinforcement. E. M. Dannenberg (Godfrey L. Cabot, Inc., Boston, Mass.).
4. Some Properties of Butyl Rubber-Carbon Black Systems. F. P. Ford and A. M. Gessler (Standard Oil Development Co., Linden, N. J.).
5. Estimation of the Wear Resistance of Vulcanized Elastomers. J. C. Burns and E. B. Storey (Polymer Corporation, Ltd., Sarnia, Ontario).
6. The Effect of Metallic Oxides on the Vulcanization of Neoprene Type W. F. H. Fritz and L. R. Mayo (E. I. du Pont de Nemours & Co., Wilmington, Del.).

DYNAMIC PROPERTIES OF RUBBERLIKE MATERIALS

Chairman, J. W. Liska, Firestone Tire & Rubber Co., Akron, O.

7. Dynamic Properties of Rubber. Robert S. Marvin (National Bureau of Standards, Washington, D. C.).
8. Correlation of Dynamic and Static Measurements on Rubberlike Materials. R. D. Andrews (Dow Chemical Co., Midland, Mich.).
9. Dynamic Mechanical Properties of Polyisobutylenes in the Audiofrequency Range. John D. Ferry (University of Wisconsin, Madison, Wis.).
10. Vibration Characteristics of Tread Stocks. K. E. Gui, C. S. Wilkinson, Jr., and S. D. Gehman (Goodyear Tire & Rubber Co., Akron, O.).
11. Velocity and Attenuation of Ultrasonic Sound in Polymers. J. L. Melchor, A. A. Petrauskas, and E. Guth (University of Notre Dame, Notre Dame, Ind.).
12. Study of High Polymeric Material by Ultrasonics. G. I. Cathers, E. D. Bailey, A. M. Buchy, and Emanual Asness (Franklin Institute, Philadelphia, Pa.).

OZONE CRACKING

Chairman, G. R. Cuthbertson, U. S. Rubber Co., Detroit, Mich.

13. Static Exposure Testing of Automotive Rubber Compounds. H. A. Winkelmann (Dryden Rubber Division, Sheller Manufacturing Corp., Chicago, Ill.).
14. Ozone in Los Angeles and Surrounding Areas. A. W. Bartel (United States Rubber Co., Los Angeles, Calif.) and J. W. Temple (United States Rubber Co., Detroit, Mich.).

15. Crack Depth Analysis of Ozone Cracking Results. JOHN S. RUGG (Gates Rubber Co., Denver, Colo.).
16. Effects of Temperature and Elongation on the Cracking of Rubber and GR-S in Ozone. G. R. CUTHBERTSON AND D. D. CUNNOM (U. S. Rubber Co., Detroit, Mich.).
17. Ozone and Sunlight Aging Studies of Carbon Black Vulcanizates. GEORGE E. POPP AND LYNN HARBISON (Phillips Chemical Co., Akron, O.).
18. Ozone Resistance of Neoprene Vulcanizates. Effect of Compounding Ingredients. D. C. THOMPSON, R. H. BAKER, AND R. W. BROWNLOW (E. I. du Pont de Nemours & Co., Wilimington, Del.).

PREPARATION OF SYNTHETIC RUBBER

Chairman, W. B. Reynolds, Phillips Petroleum Co., Bartlesville, Okla.

19. Synthetic Rubber Preparation—A Review of Important Polymerization Processes. R. L. BEBB (Firestone Tire and Rubber Co., Akron, O.).
20. Viscosity-Conversion Relationships in Sulfur-Modified Polychloroprenes. W. E. MOCHEL (E. I. du Pont de Nemours & Co., Wilmington, Del.).
21. Polymerization Rates in Emulsion Systems. MAURICE MORTON, P. P. SALATIELLO, AND H. LANDFIELD (University of Akron, Akron, O.).

PROPERTIES OF SYNTHETIC RUBBER

Chairman, J. D. D'Ianni, Goodyear Tire & Rubber Co., Akron, O.

22. Relationship between Molecular Structure and Physical Properties of Synthetic Rubber. S. D. GEHMAN (Goodyear Tire and Rubber Co., Akron, O.).
23. Butadiene-Styrene Rubbers. Some Effects of Polymerization Temperature and Molecular Weight. J. R. BEATTY (B. F. Goodrich Co., Research Center, Brecksville, O.) and B. M. G. ZWICKER (B. F. Goodrich Chemical Co., Cleveland, O.).
24. Viscosity-Molecular Weight Relation for Polybutadiene. Effect of Polymerization conditions which Influence Branching and Cross-Linking. B. L. JOHNSON AND R. D. WOLFANGEL (Firestone Tire & Rubber Co., Akron, O.).
25. Structure of Alkali Metal-Catalyzed Butadiene Polymers. A. W. MEYER, R. R. HAMPTON, AND J. A. DAVISON (United States Rubber Co., Passaic, N. J.).
26. Polysulfide Polymers. Low-Temperature Properties. E. M. FETTES, J. S. JORCZAK, R. L. KNARR, AND P. E. MEISS (Thiokol Corp.).

NATURAL AND SYNTHETIC LATEX

Chairman, L. A. Wohler, Firestone Tire & Rubber Co., Akron, O.

27. Review of Recent Progress in Latex Technology. E. A. MURPHY (Dunlop Tire & Rubber Co., Birmingham, England).
28. Latexes of Flexible Synthetic Polymers. B. M. G. ZWICKER (B. F. Goodrich Chemical Co., Cleveland, O.).
29. Some Factors in the Prevulcanization of Latex. H. B. TOWNSEND, P. G. COOK, AND P. A. COFFIN (General Latex & Chemical Corp., Cambridge, Mass.).

30. Physical Properties of Films from Mixtures of Natural and Synthetic Rubber Latex Blends. R. M. PIERSON, R. J. COLEMAN, T. H. ROGERS, JR., D. W. PEABODY, AND J. D. D'IANNI (Goodyear Tire & Rubber Co., Akron, O.).
31. Water Vapor Permeability and Sorption of Hevea Latex Films. WILLIAM W. BOWLER (Firestone Tire & Rubber Co., Akron, O.).
32. Mechanical and Chemical (Zinc Oxide) Stability Tests. C. O. MISERENTINO (Dunlop Tire & Rubber Co., Buffalo, N. Y.).
33. Studies on the Yellow Fraction of Latex. G. E. VAN GILS (Indonesian Rubber Institute, Bogor, Indonesia).
34. GR-S Latexes in Foam Rubber. LEON TALALAY (Sponge Rubber Products Co., Shelton, Conn.).

NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY. Volume XIV, 1950. Edited by T. J. Drakeley. Published by W. Heffer & Sons, Ltd., Cambridge, England, for the Institution of the Rubber Industry, 12 Whitehall, London S. W. 1, England. Cloth, 7½ by 9¾ inches, 120 pages. Price 1/1/10.—Following the format of previous editions, this book comprises articles on developments during 1950 both generally and in the fields of planting and production of natural rubber; properties, applications, and utilization of latex; physics and chemistry of rubber and its derivatives; synthetic rubber; testing equipment; fibers and fabrics; properties of vulcanized rubber; tires; belting; hose and tubing; cables and electrical insulation; mechanical goods; toys and sporting goods; surgical goods; proofed goods; solvents and cements; cellular rubber; hard rubber; flooring; processing and materials; and machinery and appliances. Name and subject indexes are included. [From the *India Rubber World.*]

RUBBER RED BOOK. 1951–52 Edition, Eighth Issue. Published by *Rubber Age*, 250 W. 57th St., New York 19, N. Y. Cloth 6 by 9 inches, 1,016 pages. Price, $7.50.—This edition of the "Red Book" continues the growth of the series, showing a total increase in number of pages, including advertisements of 86 over the seventh issue. This increase in pages is reflected by corresponding increases in the various sections of the book. The general organization and classification system remains the same, but there are several changes: the listing of classified rubber products has been improved by a code numbering system; laboratory and testing equipment has been separated from regular machinery and equipment; a listing of the ORR copolymer plants has been included in the section on synthetic rubbers; and the scrap-rubber section now contains a classified list of scrap rubbers.

The directory includes sections on rubber manufacturers in the United States and Canada; rubber machinery and equipment; accessories and fittings; rubber chemicals and compounding materials; fabrics and textiles; natural rubber and related material; synthetic rubbers and rubberlike materials; reclaimed rubber; scrap rubber; latex; miscellaneous products and services; consulting technologists; branch offices and sales agents; trade and technical organizations; educational courses in rubber chemistry and technology; technical journals; who's who in the rubber industry; and both subject and advertiser's indexes. [From the *India Rubber World.*]

PHYSICO-CHIMIE DU LATEX. W. Kopaczewski. Dunod, 92 Rue Bonaparte (VI), Paris, France. 1951. Paper, 6½ by 10 inches, 169 pages.—No systematic research work has yet been carried out on the colloidal equilibrium of latex,

and hardly anything is known about the mechanism of the physical or chemical factors capable of disturbing this equilibrium, the author points out in his foreword. For eight years he has studied various latexes, more particularly that of *Euphorbia resinifera*, to determine their physicochemical characteristics, and results have been compared with existing fragmentary knowledge and collected in this monograph, which the author claims is the first attempt at a physicochemistry of latex. The book also includes hitherto unpublished personal researches.

It is divided into three parts: generalities, conditions of stability, and analogies. The first part has two chapters. The first briefly discusses the latex-bearing individuals of no fewer than 20 families of plants; the second chapter takes up the physical and colloidal characteristics of latex.

Of the three chapters in part two, the first treats of the phenomena of gelling and gels (the author includes coagulation and coagula) and the physical, mechanical, and chemical agents used in gelling; the second chapter deals with the phenomena, experimental conditions, and mechanism of disjunction (separation into phases or fractions); the third chapter covers stabilization.

In part three, plastomers and elastomers are treated, and, finally, simple and complex biocolloids. An extensive bibliography concludes the work, which, however, contains no reference notes nor indexes. [From the *India Rubber World.*]

AN INVESTIGATION ON THE TECHNICAL CLASSIFICATION OF INDONESIAN RUBBERS. A. G. J. Arentzen and W. den Breejen. Indonesian Institute for Rubber Research, Bogor, Java.—I. METHODS OF TESTING. No. 8/51. 6 pages.—Methods for testing rubber are described which are used at present on Indonesian plantations for the purpose of technically classifying crude natural rubber. They are based on methods initiated by French rubber technologists, but in some cases changes in these methods have been made to make use of apparatus available at the plantations and also to bring the procedures more in line with those used in American industry. Homogenizing is done on a cold laboratory mill, and the samples are kept under normal tropical conditions. In testing for Mooney viscosity, a reduced time of shearing, two minutes at first and three minutes in the more recent tests, was used because of a lack of instruments to handle the large number of samples. For tension testing, the A. C. S. formula No. 1 was used, but the ingredients were added as a powder blend. The mixing cycle was 12 minutes, and the compounded stock was stored 20 to 24 hours in the dark at temperatures 22 to 32° C at a relative humidity of about 65 per cent. Two cures were made, 40 and 80 minutes at 127° C, of sheets five mm. thick, from which rings were punched. Storage conditions of the vulcanizates were similar to those of the compounded stock. Testing was on a Schopper tensimeter with automatic recording, and the force was read at 665 per cent elongation of the inner circumference (equivalent to 600 per cent on dumbbell specimens), and the results are reported as 600 per cent modulus.

II. RESULTS OF A SURVEY OF EXPORT, NOVEMBER 1914. No. 9/51. 7 pages. Tables and graphs.—Many tables of data and graphs illustrate the results of tests on various grades of rubber produced on the plantations of Indonesia. About 21 per cent of the rubber exported in November, 1949, considered a normal month, was examined. Less than 4 per cent of this rubber has a fast rate of cure, and nearly half is slow curing. About 15 per cent has a low Mooney viscosity, and 40 per cent a high viscosity. [From the *India Rubber World.*]

MEDICAL PROBLEMS ENCOUNTERED IN THE MANUFACTURE OF AMERICAN-MADE RUBBER. (Safety Reprint: Rubber No. 1.) By Dr. Rex H. Wilson, Dr. Glenn V. Hough, and William E. McCormick. National Safety Council, 425 North Michigan Ave., Chicago 11, Ill. 8½ × 11 in. 8 pp.—This paper deals with medical experiences encountered in the manufacture of the butadiene type of synthetic rubber. The ingredients known or suspected to cause health problems are discussed in some detail. Pathological and laboratory findings are discussed, as are methods of treatment and methods of detection. Toxicological properties, results of overexposure, and prophylaxis are described. The article also attempts to review and coordinate the current literature with the authors' personal experiences and observations. [From the *Rubber Age* of New York.]

INDUSTRIAL WASTES: THEIR CONSERVATION AND UTILIZATION. By Charles H. Lipsett. Published by the Atlas Publishing Co., 425 West 25th St., New York 1, N. Y. 6¼ × 9¼ in. 317 pp. $5.00.—A comprehensive analysis of all the important industrial wastes, their vital role in the economic life of the country and a description of the origins of the various wastes make up this volume. Methods used in collecting wastes, marketing procedures, recovery processes and utilization by industry are outlined. Written in an easy-to-read style, the book ranges over a wide field of essential wastes including rubber, chemicals, plastics, metals, textiles, leather, etc., as well as organic wastes, paints and solvents, agricultural wastes, and others. Chapters of the book are devoted to rubber scrap, rubber scrap processing, and foam rubber. [From the *Rubber Age* of New York.]

DIRT CONTENT OF CRUDE HEVEA RUBBER. K. F. Heinisch and G. J. van der Bie, Indonesian Institute for Rubber Research, Bogor, Java. I. DETERMINATION OF DIRT CONTENT. No. 4/51. 11 pages.—After a short general survey of the present methods used for dirt in rubber, an improved gravimetric method is described, which has been found suitable for routine determinations. A distinction is made between the "insoluble" portion, which is termed "absolute" or "total" dirt, and the "harmful" dirt; the latter is classified as the mechanical impurity which is retained on a 325-mesh screen.

II. AVERAGE DIRT CONTENT OF TRADE GRADES. No. 7/51. 14 pages. Illustrated.—A survey of the dirt content in various trade grades of crude rubber shows that there is little relation, on the whole, between dirt content and the trade grades of rubber. Rubber produced under the greatest of care is free from harmful dirt, but contains from 0.15 to 0.40 per cent total dirt, which is made up of natural components of the latex. The harmful dirt content in the better grades of rubber averages about 0.10 per cent and is more than 0.5 per cent in some of the lower grades. The dirt in the lower grades is generally of a much coarser structure.

IV. INFLUENCE OF PACKING AND BALE COATING. No. 10/51. 7 pages.—Smoked sheet as a wrapping material absorbs dirt particles more readily than crepe or blankets, and it is easier to brush off (either wet or dry) dirt particles from crepe than from smoked sheet. Cloth wrappings result in absorption of great amounts of fibers which are difficult to remove from the rubber. Bale coatings not only prevent bales from sticking to each other, but protect the bales from absorbing dirt and also aid in their cleaning. [From the *India Rubber World.*]

ASTM Standards on Rubber Products (With Related Information). American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. May, 1951. 654 pages. Price, $5.—This latest edition of committee D-11's standards for rubber products presents in compact form the 100 testing methods and specifications developed by the Committee. Many of these standards have been revised recently, and the book also includes two emergency alternate provisions for friction tape (D 69-48T) and rubber insulating tape (D 119-48T). [From the *India Rubber World.*]

Rubber and Its Derivatives as Protective Coatings for Metals. By R. F. Reynolds. Andre Rubber Co., Ltd., Kingston By-Pass, Surbiton, Surrey, England. $6\frac{1}{4} \times 8\frac{1}{2}$ in. 16 pp.—Rubber as a protective coating for metals is discussed in this paper, which for this reason is not primarily concerned with the elastic properties of rubber, but with its chemical inertness and resistance to abrasion. The use of soft natural rubber and ebonite as protective coatings are discussed, the use of rubber-lined equipment is outlined, and the use of rubber for impact and abrasion resistance is fully covered. Photographs depicting rubber linings and coverings as they are used in industry, aboard ship, etc., are included. [From the *Rubber Age* of New York.]

THE RUBBER HYDROCARBON IN FRESHLY TAPPED HEVEA LATEX *

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INTRODUCTORY

Characterization of rubber hydrocarbon by intrinsic viscosity, osmotic pressure, light scattering, and sedimentation and diffusion methods has yielded considerable information on the size and shape of rubber molecules in solution, and has established that the rubber hydrocarbon of Hevea brasiliensis as normally handled in Europe and America comprises a series of polymer homologs with average molecular weight in the region of 500,000 to 1,000,000 and with a broad distribution of molecular weight from well over 1,000,000 down to less than 100,000. This paper summarizes the results of investigations recently carried out in Malaya to characterize the rubber hydrocarbon in fresh Hevea latex with respect to its molecular weight, as obtained by viscometric and osmotic measurements, and its molecular-weight distribution as revealed by fractionation. Fuller details are in course of publication elsewhere[1].

THE SOLUBILITY OF RUBBER HYDROCARBON OF FRESH LATEX

It is well known that coagulation of ammonia-preserved latex after importation into the consuming territories yields rather hard rubber of which only a small proportion can be brought into solution in hydrocarbon solvents (air being excluded), in contrast to the behavior of smoked sheet and of crepe rubber, of which a considerably greater proportion is soluble[2]. Attempts to extract the rubber phase from ammoniated latex by shaking it with a rubber solvent have also proved unsuccessful, only small portions of rubber passing into solution, while the rest of the latex forms with the solvent a swollen gelatinous emulsion.

The rubber content of fresh latex, however, passes readily into solution when latex is shaken with a considerable volume of benzene (not less than 100 cc. per cc. of latex), the water content of the latex becoming efficiently dispersed. Partial concentration of these solutions under reduced pressure at 30° to 35° C effectively removes the dispersed water and gives clear homogeneous solutions containing a trace of suspended insoluble nonrubber substance readily removed by settling or filtration. Benzene-soluble components of the nonrubber substances originally present in the latex are of course also present in these solutions.

Alternatively, homogeneous solutions of the rubber content of latex in three-component systems containing the water phase of the latex can be obtained by shaking fresh latex with two-component solvents containing both hydrophobic and hydrophilic components such as hydrocarbon-alcohol or hydrocarbon-

* An original contribution. This paper was presented at the 12th International Congress of Pure and Applied Chemistry, New York, N. Y., September 10–13, 1951.

pyridine, following the vistex techniques developed for latexes of synthetic polymers by Baker and Kolthoff[3]. Contemporaneously with the present work, van Essen[4] described a vistex solution method for fresh latex, using a toluene-pyridine mixture, the latex being stabilized by a nonionic stabilizer, and this mixture gave almost instantaneous solutions of fresh latex. Since all vistex mixtures contain a highly-polar component which may influence the shape and hence the intrinsic viscosity of rubber molecules in solution, or which may even dissolve a rubber which is lightly cross-linked by polar forces, it seemed preferable in investigations involving measurements of intrinsic viscosity to use only nonpolar solvents and to remove the water phase by partial concentration as described above. Under tropical conditions benzene proved to be the best solvent from the points of view of availability and freedom from peroxidation. Vistex solvents (likewise based on benzene) proved very suitable for fractionation experiments and, as will be seen later, possess certain advantages from the point of view of elimination of nonrubber impurities.

Although the rubber hydrocarbon in fresh latex is so easily dissolved on shaking with a rubber solvent, the extraction of liquid latex or vacuum-dried fresh latex films with purified petroleum ether in absence of oxygen, and under conditions avoiding agitation or disturbance of the rubber, revealed the presence of 20–70 per cent of a gel component, even when the latex was extracted from the tree by a new technique[5], whereby contact with air or exposure to light was avoided. The gel remained in the extraction flask in the form of small flocculent particles suspended in the solvent, accompanied by some greatly swollen gelatinous substance in the case of the rubbers of high gel content. Most of the gel dispersed into a cloudy "solution" when the flask was gently agitated: thus exhibiting behavior similar to that of the microgel component of GR-S synthetic rubber[6] and suggesting that the gel in Hevea latex also consists of microgel, *i.e.*, hydrocarbon material cross-linked within the latex particles and, consequently, of colloidal dimensions, in contrast to the insoluble macrogel component of smoked sheet, which does not disperse with gentle agitation and which is accordingly believed to be more extensively cross-linked.

INTRINSIC VISCOSITY OF RUBBER OBTAINED FROM LATEX

The viscosity of rubber from fresh latex was investigated by using solutions prepared in the various ways outlined above. Three different intrinsic viscosities[7] were measured:

(1) The "Latex Solution Viscosity" (L.S.V.) obtained from a dehydrated solution in benzene, prepared direct from latex. The concentration was that of the total solids content, which was generally some 10 per cent greater than the true rubber content.
(2) Intrinsic viscosity of the rubber precipitated by addition of excess methanol to a dehydrated solution of latex in benzene, dried in vacuo, and redissolved by shaking with benzene.
(3) Intrinsic viscosities of the sol and gel components of rubber, the former measured on a solution obtained by extraction of dried latex films without agitation, and the latter measured on solutions prepared by shaking the remaining gel component with benzene.

Effect of nonrubbers on intrinsic viscosity.—The ratio of the intrinsic viscosity of the precipitated rubber, evaluated as item (2) above, to that of the latex solution, was of a considerably higher order (1.25 to 1.4) than that expected if

the nonrubber substances present in the latex solution functioned solely as low-molecular diluents. This discrepancy could be only partially accounted for by failure of low-molecular components of the rubber to be precipitated under the standardized conditions of Table 1.

TABLE I

PRECIPITATION OF RUBBER FROM LATEX SOLUTIONS BY A STANDARD PROCEDURE (ADDITION OF AN EQUAL VOLUME OF 30 PER CENT BENZENE IN METHANOL)

Intrinsic viscosity of			
Latex solution	Redissolved pptd. rubber	Ratio	Percentage rubber pptd.*
4.8	7.12	1.5	69
5.4	7.57	1.4	75
4.9	6.71	1.4	79
6.3	8.47	1.3	85
5.6	7.37	1.3	87
7.2	9.18	1.25	87
5.0	6.50	1.3	87.5

* Expressed as percentage of total solids in solution.

Evaporation (in vacuo) of the solution remaining after precipitation of the rubber from a latex solution, resolution of the residue in benzene, and addition of the solution to a benzene solution of the precipitated rubber closely restored the original latex solution viscosity showing that no increase in molecular aggregation of the rubber itself could have occurred as a result of precipitation and drying. Consequently, since the intrinsic viscosity increase on precipitation exceeded that due to the purely additive effects of the eliminated nonrubber and low viscosity components, the observed increase was attributed to a depression of viscosity in the solution obtained from latex due to the polar character of the nonrubber substances eliminated from the rubber on precipitation. This was confirmed by addition of such substances to a solution of a precipitated rubber. Thus the addition of 10 per cent of the acetone-soluble components of rubber reduced the intrinsic viscosity as much as 15 per cent in one instance.

Intrinsic viscosity of sol and gel rubbers.—In agreement with Baker's observations on GR-S microgel[6], the intrinsic viscosities of solutions of dispersed Hevea gel rubber were generally rather lower than the viscosity of the separated sol rubber, in so far as it was possible to estimate the former in the presence of the considerable amount of insoluble nonrubber substances concentrated in the gel. To what extent cross-linking in gel rubber is due to its association with these nonrubber substances, or to oxygen-bridging, has not hitherto been determined with any certainty, owing to the practical difficulties of establishing the existence of primary linkages in the presence of nitrogenous and mineral impurities. It is known that, even after extensive purification under conditions precluding chemical fission of bonds, a small amount of nitrogen (0.01 to 0.03 per cent) remains firmly bound with the rubber[8], and it is not unreasonable to suspect that these small amounts of nitrogen, or of oxygen or other hetero-atoms, if efficiently combined in cross-linkages, could account for the peculiar solubility characteristics of gel rubber. Purification of latex in fact only brought about a partial reduction in the gel content (Table II), showing that the bulk of the nonrubbers originally present outside the latex particle were not involved in the structure of the gel.

The gel components of these purified rubbers could not be dissolved by shaking, but since the intrinsic viscosities of the sol components exceeded those of the total rubbers, it was clear that the intrinsic viscosities of the gel components were again relatively lower than those of the sol rubbers.

TABLE II

EFFECT OF PURIFICATION OF LATEX ON GEL CONTENT

Source of latex	Residual nitrogen in dry rubber (%)	Before purification (%)	Gel after purification	Intrinsic viscosity of	
				Original rubber	Sol component
Tree 15	.04	71	41	7.12	8.42
Tree 14	.04	27	20	7.21	7.4

Dependence of intrinsic viscosity on tree, tapping date, duration of tapping and storage.—Observations on some selected trees during rather more than a year showed a small but statistically significant day-to-day variation within each tree, with a very much larger difference between trees of different clones. It is noteworthy that no general trend or seasonal fluctuation was observed, even during the period of defoliation and new leaf-growth during which latex yields always suffer considerable reduction. A striking feature of the observations on fresh latex was the high order of magnitude of intrinsic viscosity revealed both in the latex solution viscosity (4.5 to 7.5) and in the rubbers ($[\eta]$ 6 to 10) precipitated from the latex solutions. This establishes clearly that the rubber hydrocarbon as it leaves the tree is already present as a high-molecular substance.

Experiment showed that the intrinsic viscosity of the rubber hydrocarbon in latex does not change significantly during the period of latex flow from the tree, nor were any significant changes observed in the latex solution viscosity of samples taken during four hours' storage after tapping, nor during a few weeks' storage of latex preserved either with ammonia or under neutral conditions with bactericide and nonionic stabilizer[9]. More prolonged storage rendered the rubber partially insoluble, so that the latex could no longer be brought into solution, nor could coagulated rubbers, which had been dried in vacuo, then be completely dissolved.

INTRINSIC VISCOSITY OF RUBBER HYDROCARBON IN LATEX, CREPE, AND SMOKED SHEET

Considerable difficulty accompanies attempts to make a reliable comparison of the intrinsic viscosities of rubbers in latex and in dried rubber. Logically this should be done only with latex freed from all nonrubber substances, but displacement of surface-active substances by soap before creaming gave a latex containing residual soap which depressed the L.S.V.; moreover, vacuum-dried rubbers from highly purified latexes were frequently partially insoluble. The most satisfactory compromise accordingly appeared to be the comparison of L.S.V. with vacuum-dried coagulum, using white fraction or multicreamed latex. Only small differences in intrinsic viscosity were then observed, not greater than could be accounted for by differences in the nonrubber content, while the intrinsic viscosities of the rubbers precipitated either from solutions of the latex or of the dried coagulum were practically identical. Furthermore, the differences between L.S.V. of unpurified latex and the intrinsic viscosity of

the corresponding vacuum-dried rubber were not very large (Table III). Preparation of smoked sheet, involving several days' exposure to air at 50–65° C, or preparation of crepe, involving some machining, slightly reduced the intrinsic viscosity (Tables III and IV).

TABLE III

COMPARISON OF L.S.V. WITH INTRINSIC VISCOSITY OF VACUUM-DRIED COAGULUM AND SMOKED SHEET

	Intrinsic viscosity of	
L.S.V.	Vacuum-dried coagulum	Smoked sheet
4.95	4.95	4.85
5.15	5.66	5.79
5.25	5.64	5.50
5.5	6.11	5.94
5.7	6.66	6.16
7.6	7.83	7.61
7.3	7.4	7.44

TABLE IV

COMPARISON OF L.S.V. WITH INTRINSIC VISCOSITY OF VACUUM-DRIED CREPE AND AIR-DRIED CREPE PREPARED FROM ESTATE LATEX

		Intrinsic viscosity of		
Incoming latex	L.S.V.	Vacuum-dried coagulum	Vacuum-dried crepe	Air-dried crepe
September 6th	6.1	6.45	5.62	5.60
September 27th	6.4	6.81	5.85	5.65
October 6th	6.0	6.25	5.90	5.63

The viscosity reduction in the crepe rubber was attributed to machining rather than to drying in air, since the corresponding intrinsic viscosities of vacuum-dried crepes were little different from the air-dried samples, whereas the intrinsic viscosities of the crepe samples were lower than those of corresponding vacuum-dried coagula.

FRACTIONATION OF THE RUBBER HYDROCARBON OF FRESH LATEX

Progressive cooling of benzene-methanol solutions of an unpurified rubber of high average intrinsic viscosity, obtained in solution at the tree, revealed the presence of a very considerable proportion of high-molecular material characterized by intrinsic viscosity (in benzene) in the region of 10 and more (Table V).

TABLE V

BENZENE-METHANOL FRACTIONATION OF A DEHYDRATED SOLUTION OF LATEX

Precipitation temperature of fraction	Total rubber in fraction (%)	Intrinsic viscosity
38.3°	17.5	Insoluble
36.2°	26	5.78 in benzene + 15% methanol
29.0°	47.5	9.94 in benzene
Residual solution	9	3.34 in benzene

Fractionation of vacuum-dried freshly-coagulated latex and of some samples of year-old smoked sheet, after preliminary removal of benzene-insoluble gel, similarly revealed the presence of a substantial proportion of high-molecular substances (Table VI).

TABLE VI

FRACTIONATIONS AFTER REMOVAL OF BENZENE-INSOLUBLE GEL

(In 70/30 benzene-methanol)

Rubber	Component	Rubber (%)	Intrinsic viscosity	Nitrogen (%)
Smoked sheet (soft rubber)	Whole rubber*	100	5.65	—
	Gel	31	—	0.94
	Fraction pptd. at 29.3°	15	11.45	0.22
	Fraction in solution	54	5.43	0.06
Smoked sheet (hard rubber)	Whole rubber*	100	Part insol.	—
	Gel	37	—	1.17
	Fraction pptd. at 29.3°	22	10.31	0.14
	Fraction in solution	41	5.45	0.03
Smoked sheet (hard rubber)	Whole rubber*	100	7.28	—
	Gel	37	—	0.94
	Fraction pptd. at 29.3°	24	10.75	0.19
	Fraction in solution	39	6.67	0.14
Vacuum-dried coagulum	Whole rubber*	100	5.46	
	Gel	63.7	—	0.51
	Fraction pptd. at 30.6°	10.2	10.78	
	Fraction pptd. at 28.5	3.2	8.23	0.14
	Fraction pptd. at 25	2.3	6.29	0.02
	Fraction pptd. at 10	5.3	2.74	0.004
	Fraction in solution	7.7	0.91	

* Acetone-extracted samples dissolved and dispersed by shaking.

A considerable volume of data on fractionation of smoked sheet rubber is already available from previous studies in Europe and America[10], and the only new aspect of the data in Table VI is in the relatively small contribution which the gel component makes to the overall intrinsic viscosity of the total rubber when the latter is dispersed (or dissolved) by shaking. Few of the American and European studies, however, have revealed fractions with intrinsic viscosity greatly exceeding 8 in benzene or 4.5 in benzene + 15% methanol, with the exception of some fractions with inherent viscosities up to 14 reported by Johnson[11].

Fractionation of Vistex solutions of latex.—An alternative approach to the problem of studying the molecular-weight distribution in rubber hydrocarbon

TABLE VII

FRACTIONATION OF A VISTEX SOLUTION * OF LATEX IN BENZENE-ISOPROPANOL

Consecutive pptn. temps. (° C)	Yield of rubber (%)	[η]	Analysis		
			% N	% Ash	%O
31.5	23	Insol.			
30.5	18	9.7	0.02	0.02	0.09
29.0	15	7.9	0.01	0.04	0.05
10	24	5.8			
Residue	20		Degraded and contaminated with nonrubbers.		

* 10 cc. of latex in 320 cc. of benzene + 80 cc. of isopropanol.

as it leaves the tree lies in utilization of the very convenient Vistex solution technique referred to earlier. A mixture of benzene with isopropanol proved eminently suitable for obtaining solutions, which were slightly hazy, of latex from which a series of fractions (Table VII), including some of a quite unusual degree of purity, were obtained by addition of more isopropanol and progressive cooling.

The nitrogenous and the insoluble mineral components of the nonrubbers, which were mainly concentrated in the first fraction, could be further reduced by removing the lutoids[12] from the latex and using the white fraction for preparing the vistex solution.

Soluble nonrubber substances became concentrated in the last (most soluble) fractions, which were discarded, since they had undoubtedly suffered some degradation during evaporation of the considerable volumes of solution involved. Unfortunately isopropanol exhibited a very great tendency to become peroxidized, which contributed toward degradation; of alternative solvent pairs benzene-ethanol or benzene-acetone were less effective in concentrating the nitrogenous impurities in the first fraction.

To verify whether there was indeed in fresh rubber a fraction of low intrinsic viscosity or whether those isolated above were cumulative degradation products, some centrifuged white fraction of latex from trees known to give soft rubber was coagulated by pouring into acetone, squeezed into a thin sheet, acetone-extracted at room temperature, and dried in vacuo. Fifty grams of the dried rubber (intrinsic viscosity 5.7) was dissolved in benzene-methanol, and a major fraction (72 per cent, intrinsic viscosity 6.96) was precipitated by adjusting the methanol concentration to 20 per cent at 30° and then cooling to 29°, leaving 23.7 per cent (isolated from solution by evaporation under reduced pressure), with intrinsic viscosity 2.47. The latter material was redissolved in benzene-methanol and again divided into two fractions by adjusting the methanol concentration to 21 per cent at 28.5°, thus precipitating 58.9 per cent, with intrinsic viscosity 3.35, and leaving in solution 34.2 per cent with intrinsic viscosity 1.25. The last fraction, a soft, plastic, tacky rubber, represented 8.1 per cent of the original acetone-extracted rubber (Found: C, 85.3; H, 11.8; ash, 0.8; N, nil; O, 1.78%). An analysis of the intrinsic viscosities in relation to the proportions of the separated fractions shows that no appreciable degradation can have occurred in these manipulations.

LOW MOLECULAR OXYGENATED FRACTIONS OF RUBBER

The finding of a fraction containing oxygen (directly determined) considerably in excess of the ash content in the above fractionation was of considerable interest, since similar fractions had been isolated from smoked sheet and pale crepe rubbers in England[13] and in the East[14], and it had not hitherto been clearly established whether such fractions were formed by oxidative degradation of rubber or whether they were originally present in the rubber in fresh latex. In the course of the present investigations several such low-molecular fractions were isolated in fractionation procedures and by diffusion. In the latter method it was found very convenient to subject the rubber to continuous extraction with the benzene-ethanol azeotrope of composition 65.2 per cent benzene (by volume) since this mixture became a solvent for rubber at temperatures above 50°, while at 20° it extracted only nonrubber components. Consequently, a progressive increase of extraction temperature between these limits provided a convenient method of extracting fractions of progressively increasing molecular weight.

Although all the rubbers examined for their content of oxygenated fractions were prepared by pouring freshly tapped latex into acetone through which a stream of nitrogen was passed, followed by acetone-extraction under nitrogen and drying under high vacuum, with the additional precaution in one instance of collecting the latex itself in a nitrogen atmosphere, the low-molecular fractions with intrinsic viscosity below 1.5 invariably contained combined oxygen in excess of that which could be reasonably accounted for in the acetone-insoluble nonrubber substance responsible for the ash contents of the fractions (Table VIII). The proportion of such fractions isolated represented up to 10 per cent of the rubber in some of the softer rubbers examined, but appeared to be substantially less in some harder rubbers.

TABLE VIII

SOME TYPICAL OXYGENATED FRACTIONS ISOLATED FROM FRESHLY PREPARED RUBBER

Method of isolation	Fraction in rubber (%)	$[\eta]$ of fraction	Analysis of fraction: C	H	O*	N	Ash
Diffusion: latex (tree 3)	1.5	0.52	87.3	11.85	0.47	0.05	0.15
collected under	2.2	0.69	87.4	11.8	0.40	—	0.15
nitrogen	1.8	1.07	87.4	11.9	0.30	0.06	nil
Diffusion: latex from previously untapped tree	5.0	1.56	85.3	11.7	2.0	0.05	0.34
Fractional pptn. of soft rubber (benzene-alcohol)	8.1	1.25	85.3	11.8	1.78	nil	0.8
Fractional pptn. of soft rubber (CCl_4-acetone)	9.1	0.70	87.2	11.9	0.65	—	0.1
Fractional pptn. of hard rubber (CCl_4-acetone)	2.2	0.77	85.8	11.65	1.6	0.05	0.6

* Oxygen content by direct determination[15].

The oxygenated fractions contained active hydrogen corresponding to 30–50 per cent of the combined oxygen if the active hydrogen was present in hydroxyl groups, and to 60–100 per cent of the combined oxygen if present in carboxyl groups, but the actual mode of combination of the oxygen has not yet been established.

INTRINSIC VISCOSITY, MOLECULAR WEIGHT AND PLASTICITY

Osmotic data obtained in Zimm-Myerson osmometers with some pure fractions of reduced molecular-weight distribution showed that osmotic molecular weights were in substantial agreement with those derived from Carter, Scott and Magat's equation[16] $[\eta] = 5.02 \times 10^{-4} M^{0.667}$. Unfortunately the Zimm-Myerson osmometer proved unsuitable for estimating molecular weights exceeding 10^6, and only a restricted range of fractions, not representing the major proportion of the rubbers, could be examined (Table IX).

TABLE IX

INTRINSIC VISCOSITIES AND OSMOTIC MOLECULAR WEIGHTS OF SOME HEVEA HYDROCARBON FRACTIONS

Intrinsic viscosity	Osmotic M.W. molecular weight	Viscosity molecular weight calculated from $[\eta] = 5.02 \times 10^{-4} M^{0.667}$
9.7	$>2 \times 10^6$	2.5×10^6
7.9	$>2 \times 10^6$	1.8×10^6
5.96	1.1×10^6	1.2×10^6
5.72		
3.80	0.8×10^6	0.6×10^6
3.73		
2.86	0.25 to 0.35×10^6	0.4×10^6

Huggins[17] has demonstrated from theoretical considerations that the value of the exponent in the generalized equation: $[\eta] = KM^{\alpha}$ depends on the shape of the polymer molecule. Any factor tending to affect shape, such as chain branching, or tending to restrict the extensibility of the molecule, such as cross-linking, can be expected to reduce the value of the intrinsic viscosity per unit molecular weight, and this would be reflected in a reduced value of α. This has been verified experimentally for a series of polybutadienes[18] and for some branched polyesters[19]. Accordingly, the value $\alpha = 0.67$ may be too high in the case of fractions containing microgel. Hence the relatively lower intrinsic viscosity of rubbers containing gel, *e.g.*, gel rubber compared with sol rubber,

TABLE X

INTRINSIC VISCOSITIES, MOONEY VISCOSITIES, AND GEL CONTENTS

Tree no.	Intrinsic viscosity of Latex solution	Intrinsic viscosity of Smoked sheet	Mooney smoked sheet	Gel content Dried latex*	Gel content Smoked sheet**
1	4.95	4.85	47	21	51
3	4.8	—	45	—	—
2	5.15	5.59	110	59	70
14	5.25	5.50	50	27	60
15	5.7	6.16	110	71	88
16	6.2	—	72	—	—
17	7.6	7.32	115	67	85

* Petroleum-insoluble gel.
** Gel insoluble in a mixture (80/20 by volume) of benzene-methanol at 30° C.

may not necessarily mean that the gel-containing rubbers have lower molecular weight. (The fraction of highest intrinsic viscosity recorded in Table IX gave a rather "ropy" solution in benzene, indicative of incipient gelation).

Although progressive mill breakdown of a given rubber produces a series of rubbers of progressively reduced intrinsic viscosity and Mooney viscosity, in which these two variables are closely correlated, it became clear in the present investigations that, while between rubbers of different origin a statistically significant correlation between plasticity and intrinsic viscosity was found in some cases, such large discrepancies were also found (Table X) that intrinsic viscosity of the fresh rubber (in benzene) could not be used as a reliable guide to the plasticity of rubber.

It appeared to be generally true that soft rubbers had low average intrinsic viscosities, with an above-average proportion of fractions in low-viscosity cate-

gories (Tables I and VIII) and also that rubbers of high intrinsic viscosity were hard, as might be expected from the implied differences in molecular weight. However, the converse was not necessarily true, and some hard rubbers had only medium or even rather low intrinsic viscosities. These were rubbers of high gel content, and their existence suggested that the plasticity of rubber is very sensitive to the presence of gel. This concept found support in an observation that artificial hardening of rubber by treating latex with benzidine, which is believed to introduce cross-linking[20], produces no significant change in latex solution viscosity.

Osmotic data revealed substantial differences between hard and soft rubbers of similar intrinsic viscosity (Table XI). Since the osmotic and viscometric

TABLE XI

OSMOTIC DATA ON HARD AND SOFT RUBBERS OF SIMILAR INTRINSIC VISCOSITY

Source of rubber	Intrinsic viscosity of: Latex solution	Intrinsic viscosity of: Pptd. rubber	Osmotic molecular weight	Mooney viscosity
Tree 1	4.9	6.96	367,000	47
14	5.2	7.07	572,000	50
2	5.2	6.60	830,000	110

data were obtained on unfractionated rubbers, the differences probably reflected different molecular-weight distributions as well as possible modification of the value of the exponent in the equation: $[\eta] = KM^a$.

Differences in hard and soft rubbers of similar intrinsic viscosity were also reflected in the magnitude of the decrease observed in passing from a good solvent (benzene) to a poor one (benzene + 15 per cent methanol), the restriction on coiling up in the poor solvent, imposed by structural influences operating in the hard rubber, giving rise to a relatively smaller reduction in intrinsic viscosity.

CHARACTERISTICS OF RUBBER IN LATEX OF UNTAPPED TREES: A NATURALLY OCCURRING MICROGEL LATEX

Since Hevea brasiliensis possesses a latex system of intercommunicating vessels, it is not surprising that withdrawal of latex at the tapping cut affects the concentration of latex over a considerable area of bark of the tree[21]. Estimates of the area of bark affected vary considerably, possibly depending on the tree, but a reduction in the rubber content of the latex at sampling points as remote as thirty feet above the tapping cut has been observed after only three tappings of a newly opened tree.

When the technique of taking samples of latex into benzene was applied to trees which had not been tapped for eight years, as well as to some twenty-year old trees which had not previously been tapped, it was immediately evident that the latex from these trees representative of several clones had very different solubility characteristics compared with normal latex since, on shaking, the rubber phase first disintegrated into small swollen particles which required considerable further shaking to bring them into solution. After dehydration the solution remained hazy and had quite low inherent viscosity (0.5 to 3), which increased slightly with concentration, and when poured from one vessel to another the solution left an insoluble rubber film on the walls of the container.

In the group of trees examined, one particular clone (P. B. 186) gave a normal latex, *i.e.*, one passing into solution after a few minutes' shaking to give concentration-independent inherent viscosities in the range 4–7.

When rubber was precipitated from benzene solutions of latexes of the above abnormal type and dried in vacuo, it could not be redissolved in either benzene or benzene-methanol. Precipitation of the rubber was practically quantitative, 88–92 per cent of the total solids (estimated by evaporation of a portion of the solution) being found in the precipitate. The nonrubber content of latex from these long-rested trees was shown to be no greater than that of normal latex; consequently the low intrinsic viscosities observed could not have been due to an abnormally high proportion of nonrubber substances in these latices.

The almost quantitative precipitation of rubber from solution and the insolubility and toughness of the precipitated rubbers proved beyond doubt that the foregoing rubbers were not of low molecular weight (*cf.* fractions of comparable inherent viscosity described in Table VIII). Even before removing residual solvent from the precipitated rubbers, difficulty was experienced in redissolving them completely, and at best only specky solutions could be obtained, containing discrete swollen gel particles. The solvent-free precipitated rubbers were swollen to a limited extent in benzene, thus resembling lightly vulcanized rubber, and estimates of the degree of swelling were obtained by visual measurements or rapid weighing of the swollen samples. These are shown in Table XII, in which *Qm* is the swelling index expressing the volume of benzene absorbed per unit volume of rubber.

TABLE XII

SWELLING INDEX OF RUBBERS FROM LONG-RESTED TREES

Preparation of samples	Clonal type	L.S.V.	*Qm*
Precipitated from solution	RRI. 514	2.1	29
Precipitated from solution	RRI. 513	1.9	28
Precipitated from solution	Av. 49	1.0	20
Acetone-extracted coagulum from purified latex	Same tree	—	20
Precipitated from solution	Av. 49	0.8	11
Precipitated from solution	Tj. 1	0.5	9

Although vacuum-dried coagula obtained from these latexes were mainly insoluble, vacuum-dried latex films could sometimes be brought into solution by violently shaking with benzene, and the inherent viscosity (1.1) of one of these solutions was found to be identical with that of the solution of the corresponding latex.

No measurable osmotic pressure was shown by latex solutions with intrinsic viscosity below 1 and of concentration less than 0.5 per cent by weight, and at the highest concentration examined (0.89 per cent) the osmotic pressure was only about 0.1 cm., indicative of enormous molecular weight.

An abnormally low ratio (1.5 to 1.8) of intrinsic viscosities in benzene and benzene-methanol compared with normal rubbers (2.0 to 2.9) indicated considerable restriction on the ability of the molecules to coil up in the poorer solvent.

All the foregoing characteristics of these abnormal latexes were consistent with the concept of a cross-linked structure confined to the individual latex particles, and such latexes have accordingly been designated as microgel latex[22].

As anticipated from the previous section, rubbers obtained from microgel latex proved to be very hard, with Williams D_{10} plasticity in excess of six units and Mooney viscosity above 120.

It follows that considerable changes must occur in the characteristics of latex and of the rubber derived from it when untapped trees are brought into regular tapping, and the change from microgel latex to a latex yielding normal rubber was complete in about ten consecutive half-spiral alternate-daily tappings. During this period the inherent viscosity of solutions of the latex increased from about 1.0 to 4 or more, while the rubber became progressively softer, providing an example of inverse proportionality between plasticity and intrinsic viscosity. Similarly, the opening of a second tapping cut above an existing tapping panel provided markedly harder rubber from the upper cut than from the lower one, with significant differences in mineral components known to affect latex stability.

The identification of microgel latex in a given part of the tree shows that latex in that part of the tree has not been withdrawn by tapping, and enables the area of a tree which supplies latex to the tapping cut to be defined. Certain high-yielding trees gave evidence of withdrawal of latex from points as remote as thirty feet above the tapping panel.

SUMMARY AND CONCLUSIONS

The rubber hydrocarbon in latex as it leaves the tree is already a high polymer, with a broad distribution of molecular weight ranging from several millions to below 100,000, with the major part of the hydrocarbon in the higher molecular weight ranges. Changes in the hydrocarbon subsequent to its leaving the tree tend to be degradative, but may also involve cross-linking reactions leading to changes in plasticity.

Structural changes in rubber attributed to restricted cross-linking have a greater influence on plasticity than on solution viscosity. A gel component (probably microgel) present in the freshly tapped hydrocarbon is of considerable importance in determining the hardness of raw rubber, but greatly complicates the interpretation of viscometric data, of which evaluation by the equation: $[\eta] = 5.02 \times 10^{-4} M^{0.67}$ only appears to be valid for gel-free rubber fractions. Plasticity and intrinsic viscosity cannot, therefore, be generally correlated, although the plasticity is influenced by the spread of the molecular-weight distribution into lower molecular weight regions.

The presence of a high proportion of microgel in latex of untapped trees and of branches remote from the tapping panel of trees in regular tapping, and the presence of combined oxygen in the low-molecular fractions of rubber hydrocarbon obtained from both normal and microgel latexes may be of interest in connection with questions of biosynthesis and metabolism of the rubber hydrocarbon of Hevea brasiliensis.

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THE APPLICATION OF RUBBER IN THE QUANTITATIVE DETERMINATION OF OZONE *

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In connection with analytical studies of smog in the Los Angeles area, it was found that a number of oxidizing substances, including ozone, are present in the air. Methods for the quantitative determination of ozone in this mixture are confusing since none of the reagents applied in the usual ozone analysis react specifically with ozone.

Rubber as a specific test for ozone has been recognized by Reynolds[1] and by van Rossem and Talen[2], the former suggesting that a quantitative measure of ozone might be developed based on its reaction with rubber. Crabtree and Kemp[3], in a detailed study of the effects of light, oxygen, and ozone on rubber, concluded that ozone is the only atmospheric component that develops this particular type of cracking on stretched rubber. Confirming this conclusion, we have identified this action only where ozone has been present. Low concentrations of ozone are in common use for comparative weather aging tests on rubber. In this paper we present results obtained by using rubber as a reagent for measuring ozone quantitatively.

It has long been known that ozone has a characteristic cracking action on raw or vulcanized rubber when the rubber is under strain in a bent or stretched condition. This cracking does not develop when the rubber is not under tension and is not accompanied by the stiffening effect characteristic of many oxidizing agents in their action on rubber. Natural and synthetic rubbers, raw and vulcanized, are sensitive to ozone when under tension. Butyl and Neoprene are more resistant to ozone than are other types of rubber.

There are a number of factors which influence the action of ozone on rubber, including:

1. Degree of stress;
2. Nature of the rubber compound;
3. Concentration of the ozone;
4. Time of exposure;
5. Velocity of the gas contacting the rubber as determined by the rate of flow and the size of the reaction tube;
6. The temperature at which the reaction takes place.

THE RUBBER COMPOUND

It is desirable to have a standard compound which is quite sensitive to ozone. The use of a particular formula is not necessary, but it is important that whatever the stock used it shall be uniform, so that the variation between samples in sensitivity to ozone is reduced to a minimum.

* An original contribution by the authors.

The following compound we have found satisfactory for standardizing purposes.

Rubber	100
Tire reclaim	125
SRF black	33
Stearic acid	1.5
Pine tar	8
Zinc oxide (F.C.)	4
Mercaptobenzothiazole	0.8
Diphenylguanidine	0.1
Sulfur	5

Cure 40 minutes at 45 lb. per sq. in. steam pressure

Well vulcanized compounds are desirable. Undercures with bloom make reading of cracking difficult. We have used rubber stocks vulcanized in a 6-inch polished square mold approximately $\frac{1}{16}$ inch thick. Before use, these slabs are exposed to the air for a few days, which removes the tack, increases the sensitivity to ozone, and aids in rendering the initial cracking more easily visible.

These vulcanized stocks are cut into uniform strips. The size 50 mm. long by 8 mm. wide has been found convenient. The rubber samples should be stored flat before using, and the wrapping removed immediately after use to prevent further action by ozone in the air. For application in the ozone test, these strips are folded in the middle and the ends are wrapped with a small copper wire at 10 mm. from the open end—forming an oblong loop in which the stretch on the rubber varies from zero to approximately 100 per cent (Figure 1-b).

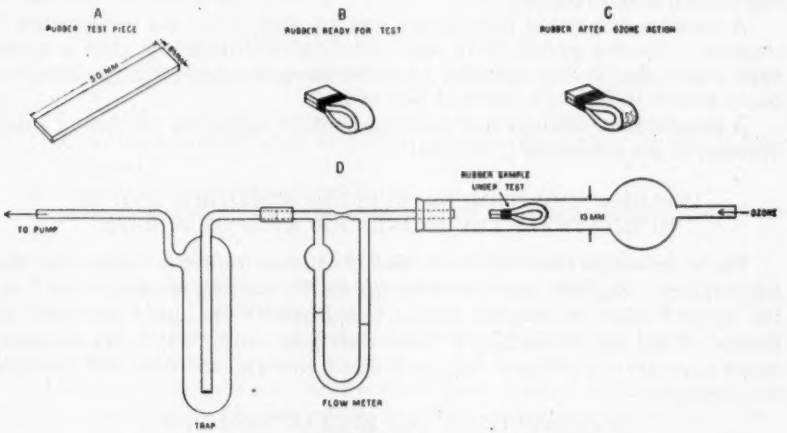

FIG. 1.

CONCENTRATION OF OZONE

Rubber under tension is highly sensitive to ozone. A 2 per cent concentration of ozone in air will crack the looped test rubber instantaneously, and will break it in two in approximately one second. On our standard test samples, 2 parts per 100 million concentration of ozone by weight at a flow rate of 1.5 liters per minute requires approximately 65 minutes to produce initial cracking. At a concentration of 26 parts per 100 million, the cracking time is 5 minutes, and at 45 parts, 3 minutes. The initial cracking time is, therefore, inversely

proportional to the concentration of ozone, and unknown concentrations may be calculated after the sensitivity of the rubber has been determined with known concentrations.

RATE OF FLOW OF GAS AND SIZE OF REACTION TUBE

The cracking effect of ozone on rubber under tension is proportional to the amount of ozone contacting the rubber surface. The action is faster in a breeze than in still air of the same composition. The same accelerating effect is obtained by moving the rubber in the gas. When a rubber sample is attached to the blade of a rotating fan, the cracking action of the air increases with the speed of the fan.

The capacity of the ozonator is a limiting factor on the rate of flow, and the flow should be kept constant in standardizing the rubber sample. In low ozone concentrations, such as air, more rapid flow may be used. We have used rates of 1.5 to 3.0 liters per minute, depending on the concentration of ozone to be measured.

With a given rate of flow, the cross-section of the tube in which the sample is mounted influences the velocity of the flow over the sample, the amount of ozone contacting the sample being greater in tubes of smaller diameter. This factor is eliminated if a definite sized tube is employed for testing. A tube (Figure 1-d) of 13 mm. diameter is convenient for moderate concentrations of ozone, and a 20-mm. tube for high concentrations. Connections ahead of the test sample should have no rubber or cork parts. Tygon tubing over glass, end to end, is satisfactory.

A vacuum pump that maintains a uniform flow of the gas to be tested is required. Electric pumps have been found more satisfactory than a water type pump, due to the variation in water pressure which often renders the pump unable to deliver a constant flow of gas.

A standardized sensitive flow meter, capable of registering the flow of small volumes of gas accurately is required.

INFLUENCE OF TEMPERATURE, OF SUNLIGHT, AND OF HUMIDITY ON THE OZONE CRACKING OF RUBBER

Our experiments show that the action of ozone on rubber increases with the temperature. Sunlight has little influence on the cracking reaction other than the indirect effect of elevation of the temperature. Humidity has little influence on the rate of cracking. These tests were carried out in the standard ozone apparatus in diffused light and direct sunlight, at room and elevated temperatures.

STANDARDIZING THE RUBBER TEST-PIECE

For a source of ozone, an ultraviolet lamp ozonator is used and the concentration of the ozone at a standard flow rate is established by neutral potassium iodide solution. The ozone output of the lamp can be modified by shielding portions of the lamp with opaque coating. The test sample is mounted in the flexed form as shown in Figure 1, arranged so that the loop portion is toward the flow of gas. Ozone is carried over the sample and the time required for initial cracking is noted. The test sample should be mounted so that the tube containing it can be readily removed and replaced, permitting preliminary examination to be made quickly. The initial cracking point is of fundamental

importance in the successful application of the method. The following suggestions may be of assistance in determining this basic reading.

When the sample is removed from the testing tube during or after the test, it can be examined in the best condition with a glass under a good light source, such as a desk lamp, pinching the sample at the loop to make any cracking show more plainly. We have used a glass of 4 magnifications. If no cracking is visible, the sample can be returned to the tube without disturbing the wrapping. It is helpful to flush the bent sample with water before the final reading to remove any dust particles that collect on the surface and interfere with the reading. Dry and examine. In the final examination, after removing the wire wrapping, it will be noted that at the point of action on the bend a dull spot appears. This effect is due to a slight crazing of the surface by the ozone, which modifies its reflecting action. It will be noted, too, that the margins of the test-piece are first affected by the ozone, and have a serrated or notched appearance where the rubber has broken at this thinnest point. The next development in the ozone action is the formation of very fine cracks on the body of the sample, shown by pinching the sample and examining it carefully with the glass. These small cracks grow larger under continued exposure. The point where both the serrated margins and the body of the sample at the convex portion exhibit beginning cracks is taken as the end point or point of initial cracking. Two or three readings should be taken in order to establish as accurately as possible the point at which definite cracking begins. Since the rubber is not stiffened by ozone, compressing the looped portion does not exaggerate the cracking.

ACCURACY OF THE METHOD

The accuracy of the rubber method of measuring ozone depends especially on:

1. Accurate standardization of rubber test-piece and proper control of this standard;
2. Accurate measurement of gas flow;
3. Proper interpretation of the time required for initial cracking.

After some experience, accuracy of ± 10 per cent can be obtained by this method.

To illustrate the practical use of the method, some results of tests on the air at Pasadena during conditions of heavy smog are outlined in Table I. The rapid changes in the ozone content under these conditions can be readily followed by this method.

In less than one hour the ozone content has increased three-fold, and this increase corresponds with observations of typical smog symptoms such as haze, eye irritation, and crop damage (discolored leaves and withered plants). These phenomena can be duplicated in fumigation rooms by the action of ozone and unsaturated hydrocarbons. The concentrations of ozone used in these experiments are well within the range of those calculated from the rubber cracking test. The sudden rise in concentration of the oxidant takes place under inversion conditions, when free exchange with the ozone present at higher elevations is excluded, and can therefore only be attributed to human activities, industrial, automobile, etc., at ground level.

Experiments on plants have shown that typical smog damage is obtained when, instead of ozone, NO_2 and sunlight in air are used for oxidation of the

TABLE I

Time ending	Minutes required	Ozone content of air as calculated from rubber cracking Parts per 100 million by weight
Nov. 27, 1950		
1. 12 Noon	30	4
2. 1:16 p.m.	22	6
3. 1:37 p.m.	17	8*
4. 2:00 p.m.	15	9*
5. 2:17 p.m.	12	11*
6. 2:35 p.m.	12	11*
7. 2:54 p.m.	14	9*
8. 3:49 p.m.	23	6
9. 4:36 p.m.	21	6
Feb. 9, 1951		
1. 11:00 a.m.	32	4
2. 11:42 a.m.	32	4
3. 12:10 p.m.	26	5
4. 12:40 p.m.	21	6
5. 1:50 p.m.	21	6
6. 2:21 p.m.	10	13*
7. 2:33 p.m.	6	22*
8. 2:45 p.m.	7	19*
9. 3:05 p.m.	7	19*
10. 3:26 p.m.	7	19*
11. 4:10 p.m.	10	13*
12. 4:38 p.m.	17	8

* Heavy smog.

olefins. Under these conditions, rubber shows cracking indistinguishable from that caused by ozone. As pointed out in a private communication by O. R. Wulf and F. E. Blacet, it is possible that the catalytic effect of the nitrogen oxides results in the building up of an appreciable concentration of ozone. The dissociation of NO_2 in the air gives rise to atomic oxygen, which, because of the great excess of oxygen, forms ozone. After the reoxidation of NO with molecular oxygen, the light reaction again produces atomic oxygen. Nitrogen oxides function, therefore, as catalysts in the production of ozone. The absence of rubber cracking with nitrogen oxides and sunlight in nitrogen atmosphere supports this hypothesis.

No rubber cracking was noticed in the presence of SO_2 and sunlight. The formation of ozone in the oxidation of SO_2 to SO_3 under influence of light is, therefore, a less likely explanation of the unusually high ozone content in the Los Angeles area.

The strong oxidizing effect of the Los Angeles atmosphere as measured by the liberation of iodine from neutral potassium iodide solution has been shown to be the summation of the action of oxidizing and reducing substances in the air. In smog air, the oxidant, consisting of nitrogen oxides, ozone, and peroxidic oxidation products of organic material, outweighs the reducing action of sulfur dioxide.

SUMMARY

A convenient rubber cracking test for ozone is described. This method serves not only as a rapid, positive means of identifying ozone in complex gas

mixtures but also gives close approximation to the quantity present. Application of the method in determining ozone in heavy smog atmosphere is shown. The high ozone concentration in these tests is attributed to ozone formation under the catalytic action of nitrogen oxides and sunlight.

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[4] Crabtree and Kemp. Ind. and Eng. Chem. Analytical Edition, 769 Dec. 1946.

DETERMINATION OF THE STRUCTURE OF RUBBERS BY INFRARED SPECTROSCOPY *

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During the formation of a molecule of synthetic rubber, diolefin hydrocarbons can unite at either the end atoms, *i.e.*, at the free linkages of a monomer unit with 1,4-configuration, or at one of the double bonds in a monomer unit with 1,2- and 3,4-configurations.

$H_2C{=}CH{-}CH{=}CH_2$	diethylene hydrocarbon (butadiene)
$-CH_2{-}CH{=}CH{-}CH_2-$	butadiene unit with 1,4-configuration
$-CH_2{-}CH(-CH{=}CH_2)-$	butadiene unit with 1,2-configuration

The proportion of the diethylene hydrocarbon units in 1,2- and 1,4-formation determines many of the technical properties of the final rubber product.

Chemical methods used until recently to determine the number of 1,2-structural units and 1,4-structural units are not only difficult, but also are insufficiently accurate.

On the other hand, the determination of the molecular structure of the monomer in a synthetic rubber by infrared spectroscopy does not offer any serious difficulties. The C—C region of vibrations ($\sim$1000 cm^{-1} was used for this purpose[1,2].

In this work, the C—H vibration band in the $=CH_2$ and $-CH_2-$ groups was used to analyze butadiene rubbers for the number of 1,2-type and 1,4-type of configurations which they contained. The spectral region in which these groups are located is much more useful in such experimental work than is the C—C region of vibration.

The proportion of 1,2-type and 1,4-type of compounds was determined by the number of side vinyl groups, $-CH{=}CH_2$, and by the number of methylene groups $-CH_2-$, according to the following relations:

$$N_{-CH_2=} = n_{1,2} \tag{1}$$

and

$$N_{-CH_2-} = n_{1,2} + 2n_{1,4} \tag{2}$$

where $n_{1,2}$ and $n_{1,4}$ are the relative quantities of elemental 1,2- and 1,4-units in 1 gram-molecule of the original monomer. $N_{-CH_2=}$ and N_{-CH_2-} denote the ratios of the number of corresponding groups to the total number of elemental units in 1 gram-molecule of the initial monomer.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Reports of the Academy of Sciences* (USSR), Physics Series, Vol. 14, No. 4, pages 452–457 (1950).

The ranges are:

$$0 \leqslant N_{-CH_2} \leqslant 1 \quad \text{and} \quad 1 \leqslant N_{-CH_2-} \leqslant 2.$$

It is necessary that the frequency and intensity used in such quantitative analysis be sufficiently characteristic and that the neighboring bands which correspond to the frequencies of other groups present in the given compound do not interfere.

In choosing a suitable spectral region, we measured the absorption spectra of the individual compounds and of the rubber for the fundamental band of the C—H vibration and for the first harmonic. The spectra for the rubbers are shown in Figures 1 and 2. The absorption coefficients for 1 cm. of carbon

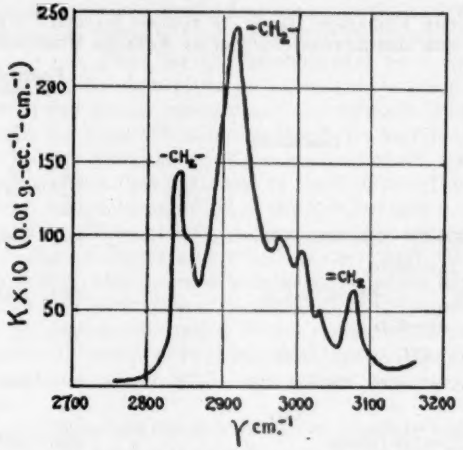


FIG. 1.—Absorption spectrum of a solution of rubber in carbon tetrachloride (fundamental tone).

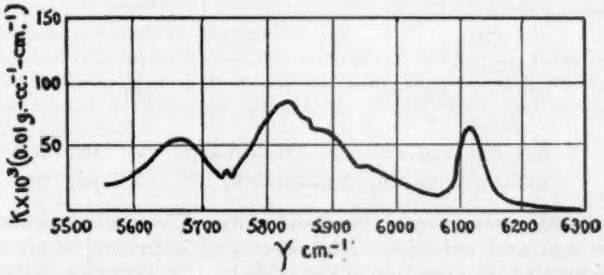


FIG. 2.—Absorption spectrum of a solution of rubber in carbon tetrachloride (first overtone).

tetrachloride solution of 0.01 g.-cc.$^{-1}$ concentration are plotted on the ordinate axis according to the Lambert-Beer law:

$$I = I_0 e^{-KCd} \tag{3}$$

and

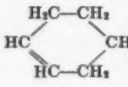
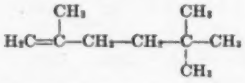
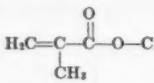
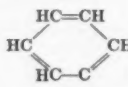
$$K = \frac{1}{Cd} \ln \frac{I_0}{I} \tag{3'}$$

where I_0 and I are the intensities of the radiation which impinges and passes through an absorbing layer of the substance of thickness d and concentration C, and K is the absorption coefficient.

The absorption spectra in the fundamental band were measured with a Perkin-Elmer spectrometer having a lithium fluoride prism, through a spectral aperture about 9 cm.$^{-1}$ wide. The spectra in the first harmonic were measured with a monochromator in which a diffraction grating filter was used. The linear scattering was 42 A mm.$^{-1}$. The experiment was conducted with an aperture of 7.5 cm.$^{-1}$. A lead sulfide photoelement attached to an alternating-current amplifier served as detector of the radiation. The light rays were

TABLE 1

POSITION OF THE VIBRATION BANDS OF THE $=CH_2$ AND $-CH_2-$ GROUPS IN THE ABSORPTION SPECTRA OF VARIOUS COMPOUNDS

Compound	Constitution	Fundamental tone			First overtone	
		$=CH_2$	$-CH_2-\nu(s)$	$-CH_2-\nu(a)$	$=CH_2$	$-CH_2-$
Biallyl	$H_2C=CH-CH_2-CH_2-CH=CH_2$	3075	2846	2919	6114	5660
Butadiene dimer		3073	2840	2916	6116	5680
Biisobutylene		3073	2870	2910	6107	5645
Allyl alcohol	$H_2C=CH-CH_2OH$	3080	2867	2925	6140	5697
Methyl methacrylate		3100	—	—	6184	—
Styrene		3081	—	—	6130	—
Octane	$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	—	2857	2905	—	5686
Heptane	$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$	—	2857	2905	—	5688

modulated with a frequency of 300 Hertz units. The measurements were corrected for scattered radiation. The spectra of individual compounds were used to determine the spectrum of the rubber. The positions of the bands in the spectra of some of the substances are given in Table 1.

From a comparison of the absorption spectra of rubbers with those of the individual compounds, it is evident that, to determine the number of $=CH_2$ and $-CH_2-$ groups, it is better to work on the first overtone (6000 cm.$^{-1}$) than on the fundamental band (3000 cm.$^{-1}$), because the spectrum of the fundamental band is compressed and the bands overlap. In the first harmonic the spectrum is more spread out, and the 6114 cm.$^{-1}$ ($=CH_2$) and 5666 cm.$^{-1}$ ($-CH_2-$) bands in butadiene rubbers are free from interference.

TABLE 2

RELATIVE INTENSITIES OF $=CH_2$ AND $-CH_2-$ BANDS

Substance	Fundamental band	First harmonic
Biallyl	1.28 0.80	2.3
Butadiene dimer	1.40 0.75	2.0
Diisobutylene	0.6	2.3
Methyl methacrylate	1.3 (?)	3.6

Furthermore, the intensity of the bands of the CH vibrations in an unsaturated group, in comparison with the intensity of the bands of the saturated groups, are considerably greater for the first harmonic than for the fundamental band. This is shown in Table 2, where the relative intensities of the $=CH_2$ and $-CH_2-$ bands are given for the fundamental band and for the first harmonic (the experimental data given in Table 2 show a somewhat different relationship between the dipolar moment and the distance between the carbon and hydrogen atoms for these vibrations in the single and double bonds).

The data above show definitely that the analysis of the unsaturated vinyl group is better made at the first harmonic of the CH vibrations (6114 $cm.^{-1}$).

The $=CH$ group cannot be analyzed at the first harmonic because of interference on this band by the combined frequencies of other groups.

The spectral region of the first harmonic of the C—H vibrations is more suitable for analysis than the region of greater wave length, since work in the former can be carried on with glass apparatus. The thickness of the samples investigated at 1 per cent concentration in this region was 5 cm.

The quantitative analyses of the rubbers in this experiment were made with the absorption bands 6114 and 5666 $cm.^{-1}$, which represent the vinyl and methylene groups.

To convert the relative number of bonds to an absolute basis, the intensity of the absorption for one bond was calculated. This was calculated from the biallyl absorption spectrum ($CH_2=CH-CH_2-CH_2-CH=CH_2$), in which the $=CH_2$ and $-CH_2-$ form structural units, as in butadiene rubbers. The biallyl spectrum is shown in Figures 3 and 4.

The effect of ring formation on the intensity of the $=CH_2$ absorption band is shown in Table 3, where the absorption coefficients for one $=CH_2$ bond in one gram-molecule of different compounds dissolved in 100 cc. of carbon tetrachloride are listed.

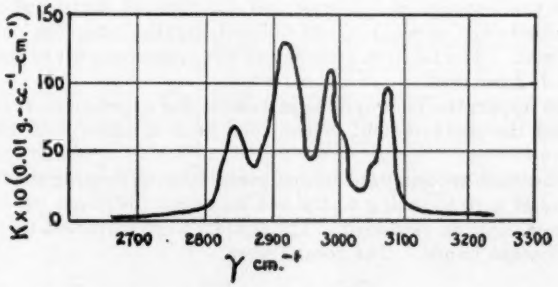


FIG. 3.—Absorption spectrum of a solution of biallyl ($H_2C:CHCH_2CH_2CH_2:CH_2$) in carbon tetrachloride (fundamental tone).

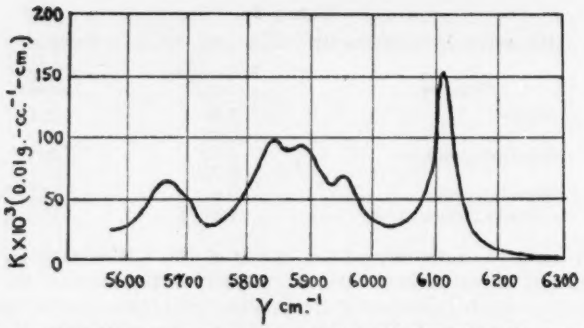


FIG. 4.—Absorption spectrum of a solution of biallyl ($H_2C{:}CHCH_2CH_2CH_2{:}CH_2$) in carbon tetrachloride (first overtone).

The number of vinyl and methylene groups in one gram-molecule representing one unit in the rubber was measured by means of the following formula:

$$N_{=CH_2} = \frac{K_{\text{rubber}}}{K_{\text{standard}}} \cdot \frac{mn}{M} \qquad (4)$$

where K_{rubber} is the absorption coefficient of the rubber solution, calculated to 0.01 g.-cc.$^{-1}$cm.$^{-1}$, K_{standard} is the absorption coefficient of the biallyl solution, calculated to 0.01 g.-cc.$^{-1}$ cm.$^{-1}$, m is the molecular weight of a monomer unit in the rubber (the molecular weight of the butadiene), M is the molecular weight of the biallyl, n is the number of groups of the given type in one gram-molecule of biallyl, and $N_{=CH_2}$ is the number of $=CH_2$ groups in one gram-molecule of the elemental unit in the rubber.

TABLE 3

EFFECT OF RING FORMATION ON THE INTENSITY OF THE $=CH_2$ ABSORPTION BAND

Compound	Value of K for one $=CH_2$ per gram-molecule
Biallyl	6.3
Butadiene dimer	6.2
Biisobutylene	6.06
Styrene	6.03

With this method we analyzed a series of about one hundred butadiene rubbers for the number of 1,2-type and 1,4-type of structural units. The values obtained $(n_{1-2} + n_{1-4}) \times 100$ differed slightly from 100 per cent., *i.e.*, by 5–6 per cent. The relative accuracy of the measurements of the number of groups was 1–2 per cent.

With the apparatus in proper adjustment, the experiment required thirty minutes, and the measurement of the coefficient of absorption ten to fifteen minutes.

For verification, we analyzed rubber sample No. 275, using the fundamental band for C–H corresponding to the $=CH_2$ group (3075 cm.$^{-1}$). Biallyl also served as a calibration standard. The graphs were corrected for interference from the adjacent bands. The results were:

	$n_{1,2}$	$n_{1,4}$	Σ	$\Delta\Sigma$
First overtone	57.5%	39.7%	97.2%	2.8%
Fundamental tone	59%	—	—	—

TABLE 4

COMPARISON OF MEASUREMENTS OF VINYL GROUP CONTENT BY INFRARED SPECTROSCOPY AND BY OZONOLYSIS

Sample no.	Percentage of butadiene units	
	By infrared spectroscopy	By ozonolysis
100	42.5	44.5
200	37.2	35.5

From this table it is evident that the experiment on the first harmonic gives a more nearly complete and accurate analysis.

The results of the measurement of the vinyl-group content by infrared spectroscopy, shown above, correspond closely with the results obtained by ozonolysis, which require three to four days to complete (see Table 4).

The method of measuring the content of $=CH_2$ and $—CH_2—$groups elaborated here also serves to measure the content of 1,2-bonds and 3,4-bonds in isoprene rubbers.

The content of butadiene units in the 1,2-structure and 1,4-structure in copolymers of butadiene and styrene can be measured by this method. The absorption spectra of isoprene and butadiene-styrene rubbers at the first harmonic are given in Figures 5 and 6.

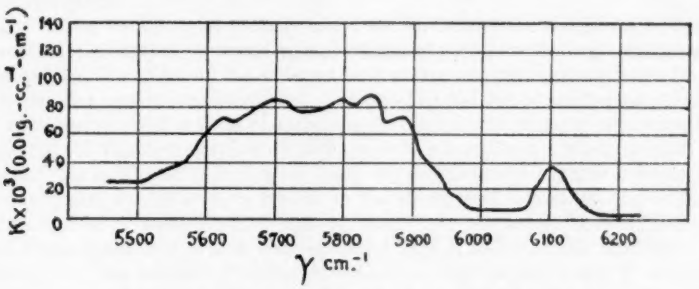


FIG. 5.—Absorption spectrum of a solution of isoprene rubber in carbon tetrachloride (first overtone).

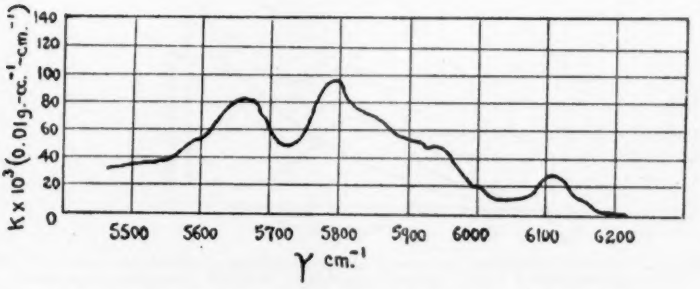


FIG. 6.—Absorption spectrum of a solution of butadiene-styrene rubber in carbon tetrachloride (first overtone).

ACKNOWLEDGMENT

This work was carried out in the Spectroscopic Laboratory of the University, with the direction and participation of V. M. Chulanovsky, to whom the author is deeply grateful.

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MOLECULAR AGGREGATION IN AMORPHOUS POLYMERS *

V. I. KASATOCHKIN AND V. V. LUKIN

We have already established the existence of two types of packing of the links of neighboring molecular chains in amorphous rubber[1]. The association of the links whose packing is characterized by a relatively dense distribution, similar to the packing of the molecules in low-molecular liquids, constitutes the liquid phase of amorphous rubber. In an x-ray diffraction diagram, this phase of the rubber shows an outer interference maximum caused by the intermolecular interference of the x-ray radiation which is coherently scattered by the adjacent links and corresponds to the average intermolecular spacing.

Another phase of amorphous rubber, formed by the association of the segments of adjacent molecular chains, of quite disordered distribution, was called the gaseous phase. The links of the molecular chains which make up this phase of the rubber, because of their irregular distribution, scatter x-rays and show no intermolecular interference effect, so the scattering is like that in molecular gases.

The dense background usually observed in diffraction diagrams of rubber, the intensity of which increases in the region of small scattering angles, can be explained by the effect of the independent scattering of the disordered links of the molecular chains of the rubber. It has the nature of scattering by a gas. The presence of such a type of molecularly disordered gaseous component is a peculiarity of the aggregation of molecules in amorphous high-molecular substances. Its existence is shown by the x-ray diffraction diagrams of amorphous high-molecular substances, in which, in the absence of low-molecular liquids, a background of independent scattering is always observed, besides the outer interference maximum which corresponds to the intermolecular spacing. The intensity I of the scattered (monochromatic) x-rays at any angle is, according to the theories developed, determined by the sum of the scattering intensities of the gaseous (I_g) and liquid (I_l) phases of the amorphous substance.

$$I = I_g + I_l$$

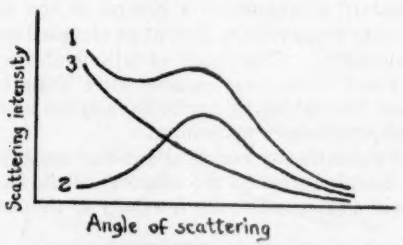

FIG. 1.—Angular distribution of scattering intensity of x-rays in amorphous polymers. Curve 1—Scattering by polymers. Curve 2—Scattering by liquids. Curve 3—Scattering by gases.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Reports of the Academy of Sciences*, USSR, Vol. 77, No. 1, pages 81–84, 1951.

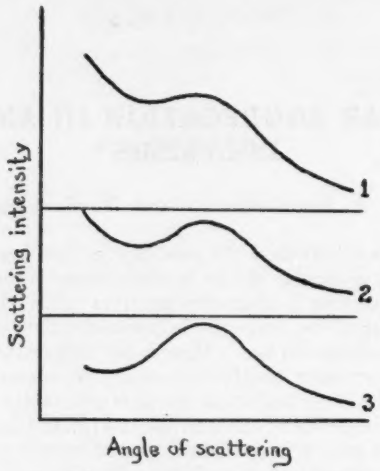

FIG. 2.—Curves of intensity for rubber at different temperatures. Curve 1—120°C. Curve 2—80°C. Curve 3—20°C.

The characteristic curve of the angular distribution of the scattering intensity of x-rays by an amorphous substance (Curve 1) is shown in Figure 1. It can be considered the sum of the liquid scattering, which is characterized by a fall of intensity down to zero in the region of small scattering angles (Curve 2), and the gas scattering, which gives a steady increase of intensity at small angles (Curve 3).

The fixed intensity for any small scattering angle beyond the limits of the interference maximum can serve as a quantitative measure of the degree of molecular disorder; in other words, of the gaseous phase of the amorphous substance.

The changes of the x-ray diffraction diagram of rubber as a function of the temperature, studied here, corroborate our interpretation of the x-ray scattering and indicate the existence of definite transition temperatures for molecular aggregation in amorphous polymers.

In Figure 2 the curves of scattering intensity of a filtered beam of x-rays from a copper target for natural rubber at temperatures of 20° ,80°, and 120° C are shown. Three x-ray diagrams of each specimen were taken in a special camera with a standard substance as a control of the temperature effect of scattering; first at room temperature, then at an elevated temperature, and then again at room temperature. The small variations observed when the rubber specimens were exposed in an x-ray camera after being heated in air are the result of oxidation of the rubber by molecular oxygen and are reflected in the somewhat increased interference maximum.

A comparison of the intensity curves shows that an increase of the temperature of the rubber sharply increases the intensity of the background, especially in the region of small angles, while the intensity of the interference maximum decreases.

The similarity between the temperature curve of x-rays scattering in rubber observed here and the change of scattering in low-molecular liquids in the temperature region above and below the critical point[2] and also in condensed gases in relation to the pressure[3] is striking.

The temperature curve of x-ray diffraction for diethyl ether studied by Noll[2] is shown in Figure 2.

When ether is heated above the critical temperature, the interference maximum gradually disappears and the curve of x-ray scattering intensity increases monotomically at small angles; showing the characteristic pattern of scattering by gases. A similar increase of background intensity and decrease of intensity of the interference maximum for rubber at increased temperatures both reflect an increased molecular disorder of the gaseous phase of amorphous rubber. Only for the given case of completely disordered distribution of the links of adjacent molecular chains and disordering in the chains, which is responsible for their free rotation, would the x-ray scattering show the absence of an outer interference maximum and be similar to scattering by a gas.

If F represents the structural amplitude factor of scattering by the individual links of the molecular chains, measured by the interference of the radiation coherently scattered by the atoms of a link, and N_g represents the number of links comprising the gaseous phase, then the intensity of independent scattering by the gaseous phase of the amorphous polymer is expressed thus:

$$I_g = PN_gF^2 \tag{1}$$

where $P = \dfrac{1 + \cos^2 2\vartheta}{2}$ is the polarization factor of the x-rays, and 2ϑ is the scattering angle.

The scattering intensity from the liquid phase of the amorphous polymer, measured by the interference of the x-rays coherently scattered by the links of the neighboring molecular chains which are closely associated can be expressed, according to the theory of scattering by liquids[4], as follows:

$$I_l = PN_lF^2\left[1 - \int_0^\infty 4\pi r^2\rho(1 - W)\frac{\sin sr}{sr}\,dr\right] \tag{2}$$

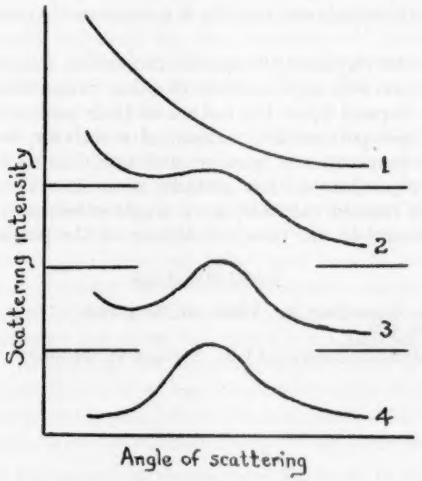

FIG. 3.—Curves of intensity for ether at different temperatures. Curve 1—210°C. Curve 2—185°C. Curve 3—105°C. Curve 4—25°C.

Here N_l is the number of links comprising the liquid, W is the probability of adjacent distribution of the links, $s = \frac{4\pi \sin\theta}{\lambda}$, λ is the wave length of the x-rays, $4\pi r^2\rho dr$ is the mass of the spherical shell of thickness dr located at distance r from any given link, and ρ is the mean density of the substance.

A general equation for the scattering intensity of x-rays in amorphous polymers can be represented in the following form:

$$I = I_g + I_l = P\left[NF^2 - N_lF^2\int_0^\infty 4\pi^2r^2\rho(1 - W)\frac{\sin sr}{sr}\,dr\right] \qquad (3)$$

where N is the total number of scattering links of the molecular chains.

In the case of completely disordered distribution of the links of the molecular chains, the probability of all the possible distributions is the same, $W = 1$, and the intensity is measured as:

$$I = PNF^2 \qquad (4)$$

For large scattering angles the integral in the general equation of intensity rapidly approaches zero, and the intensity too becomes equal to the scattering intensity of the completely disordered gaseous state of the polymer, which is measured according to Equation 4.

For small angles, this integral approximates unity, and the intensity of the liquid phase of scattering returns to zero, $I_l = 0$.

The total intensity is determined by the scattering of only the gaseous phase of an amorphous polymer:

$$I = PF^2(N - N_l) = PN_gF^2 = I_g$$

The natural obstacles to the dense packing of all the links of adjacent molecular chains are the cause of the peculiar molecular aggregation in amorphous polymers. The same obstacles to the packing of large molecules are likewise the cause of incomplete crystallization of these polymers. x-Ray analysis shows that a crystalline polymer usually is a mixture of amorphous and crystalline phases.

It follows that the physical-mechanical properties, *e.g.*, for example elasticity, modulus, etc., as well as a number of other properties of high-molecular substances, which depend upon the nature of their molecular aggregation, for example, density, gas permeability, chemical reactivity, etc., are determined essentially by the proportion of gaseous and liquid phases of the amorphous polymer. This proportion, as has already been shown[1], varies for different polymers, does not remain constant for a single substance, and depends both on external factors and on the previous history of the polymer.

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VOLUME CHANGES IN THE STRETCHING OF VULCANIZED NATURAL RUBBER *

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The significance of the problem.—Previous studies[1] of the volume changes which accompany the extension of vulcanized natural rubber have shown that, using a compound as free as possible from mineral fillers, an elongation of at least 200 per cent can be attained without the volume changing by more than 0.2 per cent. At higher elongations, the volume diminishes, a phenomenon which can be quantitatively associated with the onset of crystallization[1]. There are, however, strong theoretical and indirect experimental reasons for believing that smaller extensions must be accompanied by finite though small expansions. The magnitude of these has been predicted[2], and in this paper their existence is confirmed by quantitative measurement.

The argument which led to the prediction of these expansions is of a very general nature, and depends essentially on the possibility of resolving the tensile force into shear stresses and a hydrostatic tension. It is this latter which causes the material to expand, and this must happen for any isotropic material. If f is the force needed to elongate the material from l_0 to l and K its compressibility, the volume expansion ΔV is given by[2]:

$$\Delta V = \tfrac{1}{3}K\int_{l_0}^{l} l\left(\frac{\partial f}{\partial l}\right)_{P,T}\cdot dl \qquad (1)$$

This equation applies as long as the material remains isotropic, and is therefore probably not seriously incorrect for the materials and elongations ($<100\%$) used in our experiments. By determining the stress-strain curve of the rubber and making use of its known compressibility, Equation (1) enables us to calculate the expansion to be anticipated.

Previous indications that this analysis is correct rest on the further argument that the whole of the increase in internal energy observed in the stretching of such a rubber arises from the expansion, the internal energy being assumed to depend (at constant temperature) only on the volume, and not on the deformation. The most careful experimental studies of the thermodynamic properties of stretched rubber[3] support this argument, and lead to two conclusions: (1) that vulcanized natural rubber stretched at constant volume would not change its internal energy, and (2) that the internal energy changes observed on elongation at constant pressure are those calculated from the volume changes given by Equation (1). Additional confirmation comes from Meyer and van der Wyk's demonstration[4] that rubber can be sheared without changes of internal energy, the result to be anticipated from the fact that a shear, having no hydrostatic component, produces no volume change in an isotropic body.

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EXPERIMENTAL

For the measurement of volume changes of the magnitude expected, *i.e.*, of the order of one part in 10,000, the dilatometric method of Holt and McPherson[1] did not appear to be sufficiently sensitive. In the present investigation the method of hydrostatic weighing was adopted. The rubber was weighed immersed in water, first in the unstrained state, and then while stretched on a suitable frame. To obtain the necessary precision, it was desirable to use as large a volume of rubber as possible, but the increase of volume beyond a certain point involved slow attainment of thermal equilibrium and also necessitated an undesirably bulky supporting frame to withstand the high tensile stresses. A compromise was effected by using 8 separate ring specimens cut from a single vulcanized sheet, mounted in parallel on the frame and having a total volume of about 6 cc. Weighings could be made to 0.1 mg., which, therefore, corresponded to 1 part in 60,000 in volume. The first experiments were made on a pure gum vulcanizate of the type used in an earlier investigation by Gee[2]. This was found to give volume changes higher by about 100 per cent

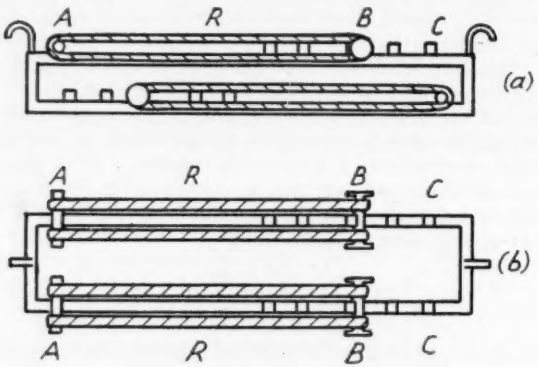

FIG. 1.—The stretching frame; (*a*) elevation, (*b*) plan.

than the theory would require. This compound contained 2 per cent of zinc oxide, and it seemed not unlikely that the excessive volume changes might have been associated with this factor, since it is well known (Jones and Yiengst[5]) that the extension of rubbers containing inert fillers gives rise to a relatively large increase in volume, usually attributed to the formation of vacuoles around the filler particles. Further experiments showed that the magnitude of the volume changes depend markedly on the zinc oxide content. Since satisfactory vulcanizates of this type could not be made without zinc oxide, attention was given to an alternative method of cross-linking which did not require the introduction of solid ingredients. In this method best quality pale crepe was cross-liked by means of di-*tert*-butyl peroxide, using a technique described elsewhere[6]. Two such compounds were investigated. Their degrees of cross-linking, or chain molecular weights (M_c) as determined by swelling in benzene and application of the Flory formula[7] with $\mu = 0.39_5$ were 4900 and 9500, respectively. Their density at 20° C was 0.920 g.-cm.$^{-3}$.

The volume measurements.—The frame upon which the rings were stretched is shown in Figure 1. The rings R of internal and external diameters approximately 3.8 and 4.2 cm., respectively, were mounted on 8 short brass rods of

diameter $\frac{1}{8}$ inch. The 4 outer ones A were fixed; the others B could be positioned against one or other of a number of suitably spaced stops C, thus giving a succession of extensions. These rods were held in place by the rubber and could be simply removed by hand when required. The frame was suspended by means of 42 s.w.g. Eureka wire from the arm of an automatic analytical balance. The water temperature was about 22° C. This was not controlled thermostatically, but differed only slightly from the temperature of the room, which was well screened from temperature fluctuations and draughts. To facilitate wetting a few drops of a detergent (Lissapol-N) were added to the water.

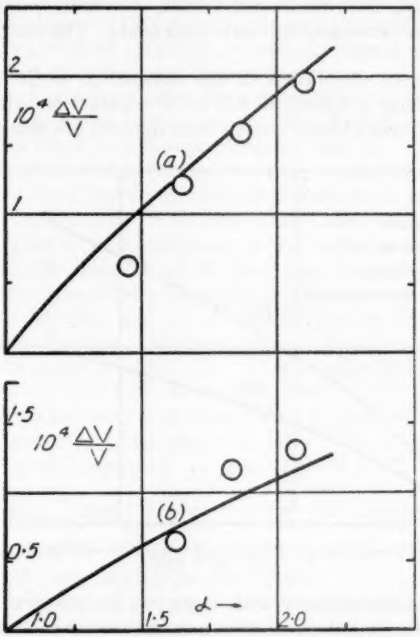

FIG. 2.—Volume changes on extension for two rubber samples: (a) $M_c = 4900$; (b) $M_c = 9500$ (curves theoretical).

The procedure adopted for the measurements was as follows. After immersion of the frame, with the specimens attached but not stretched, in the water bath, about 15 minutes was allowed for thermal equilibrium to be established before recording the weight. The rings were then quickly stretched to the lowest extension, and after a few minutes the weight was again taken. Finally the rings were relaxed and the weight again determined. For the unstrained weight, the mean of the initial and final readings was taken. The process was repeated for the same strain, and, in all, at least six but usually eight readings of the required change in weight were taken; from these the average values of volume change for this strain were derived. During the time taken for a set of readings, there was no appreciable change in the temperature of the water bath. The series of readings was then repeated at the higher extensions using the same rubber samples.

The results for the two differently cross-linked rubbers are represented in Figure 2 in terms of the relative volume change $\Delta V/V$ as a function of the extension ratio $\alpha(= l/l_0)$. The extension ratios were calculated on the internal diameter of the rings.

The tensile measurements.—The force-elongation curves were measured on two of the rings actually used for the determination of the volume changes. The length was measured to 0.5 mm. by means of a scale, and the tensions derived from the deformation of a calibrated flat steel spring. The rings were supported on brass rods of the same diameter as those fitted to the frame. The data obtained are shown in Figure 3. There was a slight difference between figures for increasing and decreasing strain, especially for the lower modulus rubber, but this was never greater than 3 per cent. The curves shown represent the mean values.

The calculation of the values of the integral in Equation (1) was carried out graphically using a figure of 5.3×10^{-6} bars^{-1} for the compressibility[8]. The theoretical volume-change curves thus derived are shown in Figure 2.

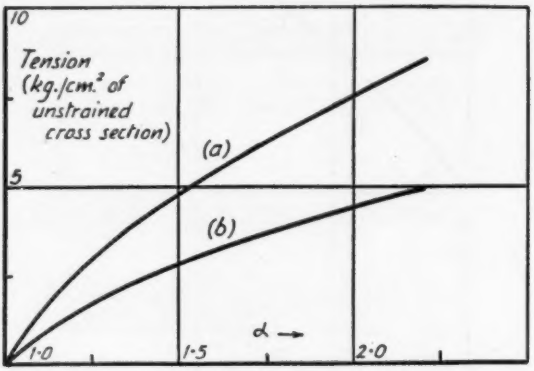

FIG. 3.—Force-elongation curves for the two rubber samples: (a) $M_c = 4900$; (b) $M_c = 9500$.

There was some uncertainty with regard to the effective extension ratio for the rings, and the calculation of this quantity with reference to the internal diameter of the rings was arbitrary. However, since the same rings and the same method of holding were used in both the volume-change and tensile experiments, any error thus introduced would have had no effect on the relative values of the theoretical and experimental volume changes at a given extension ratio. In any case the accuracy of the tensile data is so much higher than that of the volume change data, that effects of this order may be neglected.

In view of the smallness of the volume change encountered, it is inevitable that the experimental errors in its measurement should be relatively large, probably in the neighborhood of 10–20 per cent. To this degree of accuracy the data are in agreement with the calculated curves over the range of extension covered, *i.e.*, up to 100 per cent extension.

DISCUSSION

The evidence presented in this paper substantiates the interpretation put forward by Gee[2] and by Meyer and van der Wyk[4] to explain the internal energy

and entropy changes which occur on stretching rubber. The conclusion to be drawn is that two distinct mechanisms are involved in the deformation: (1) a deformation of the molecular network, without change of volume, giving a negative entropy without change of internal energy for all extensions, in accordance with the basic assumptions of the statistical theory, and (2) a bulk expansion against intermolecular forces, due to the hydrostatic component of the applied stress, and giving rise to an increase of internal energy, with a corresponding increase of entropy. It should be repeated that the existence of the second mechanism, leading to an increase of volume, can be inferred from the fact that the material is compressible and initially isotropic; that it should have been overlooked in some earlier thermodynamic studies is perhaps not surprising in view of the smallness of the volume changes in question. What is surprising at first sight is that such relatively minute changes in volume should give rise to important internal energy and entropy changes.

It should be noted, however, that the contribution of the volume-change mechanism to the total stress or free energy of deformation is negligible, as may be seen from at least two independent arguments. (1) It has already been shown mathematically[2] that if a rubber, after extension at constant pressure, is compressed at fixed length to its original unstrained volume, the tension remains practically unchanged. This means that the force-extension relation is essentially unaffected by the existence of the volume-change mechanism. (2) The work done by the applied tensile stress may be analyzed into two components, (*a*) the work done by the hydrostatic component of the stress in producing the change of volume, and (*b*) the work done by the shear stresses in producing the change of shape. Of these, it may be shown that in a typical case (*a*) is very small compared with (*b*). The effective hydrostatic tension is numerically equal to one-third of the tensile stress[2]. For one of the rubbers examined, the hydrostatic tension at 50 per cent elongation was about 2.5 kg. per sq. cm. and the corresponding expansion $\Delta V/V$ was 1.25×10^{-4}, giving a contribution to the work (assuming ΔV proportional to P) of $1.5_6 \times 10^{-4}$ kg. cm. per cc. of rubber. The total work done by the applied force is $\int_{l_0}^{l} f \cdot dl$, which for an extension of 50 per cent was $\sim$1.5 kg.-cm. This is about 10,000 times that due to the volume-change mechanism (*a*). It follows, therefore, that the latter makes no significant contribution to the total elastic stress.

This result may be regarded as a direct consequence of the fact that the bulk modulus of a rubber is higher than the Young's modulus by a factor of 10^4. The dimensional changes associated with the hydrostatic tension are therefore smaller, by a factor of this order, than the total dimensional changes accompanying the tensile stress. (Contrast the behavior of a "hard" solid, for which the two moduli are of comparable magnitude.)

From these arguments it must be concluded that the existence of an internal energy change on deformation does not necessarily imply that the mechanism with which the internal energy change is associated makes a significant contribution either to the elastic stress or to the elastic deformation.

The comparatively large internal energy changes found in the early stages of the extension of rubber may be regarded as arising from the expansion of the material against the internal pressure, which for natural rubber is about 4000 kg. per sq. cm. It, instead of a tensile stress, one applies a unidirectional compressive stress, the volume is reduced, and the sign of the internal energy change is reversed. The network entropy change is, of course, still negative. The

total entropy change is, therefore, negative for all values of compression; in particular the thermoelastic inversion phenomenon, observed on extension[9], whereby the stress-temperature coefficient and the entropy of deformation change sign (at about 10 per cent extension) does not appear. In shear also this effect is absent, but in this type of strain there is no volume change, and consequently no internal energy change.

It follows, therefore, that the changes in internal energy and entropy which accompany the elastic deformation of any material do not necessarily yield direct information regarding the mechanism of deformation, but must be interpreted with considerable caution and in the light of all the relevant facts. The analysis discussed in this paper appears to account in a natural way for the phenomena exhibited by amorphous rubber subjected to relatively small strains. It is, however, only valid for isotropic materials, and cannot therefore be applied to highly extended rubber, in which the anisotropy due directly to the strain may be enhanced by crystallization. In this region the evidence of Wood and Roth[10] indicates that the negative internal energy and entropy changes due to crystallization completely obscure the primary effects due to the elastic network. Similar or even greater difficulties may arise in the investigation of highly-oriented crystalline fibers, such as wool[11], hair[12], Nylon[11], and cellulosic materials[13], for which attempts have been made to interpret the thermoelastic phenomena. If, as often happens, the fiber is hygroscopic, there is the added difficulty, to which Woods[14] has drawn attention, that the water absorption may be a function not only of the temperature but also of the stress.

SUMMARY

Measurements are presented of the volume changes accompanying small ($\gg 100\%$) elongations of vulcanized natural rubber completely free from undissolved particles. The small expansions found agree with those calculated from the known compressibility of rubber and the hydrostatic component of the stretching force. It is pointed out that this volume change mechanism applies generally to any isotropic material, and does not contribute significantly (in rubber) to the tensile stress.

ACKNOWLEDGMENT

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HEATS OF SOLUTION AND SWELLING OF SOME SYNTHETIC HIGH-MOLECULAR COMPOUNDS *

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Application of the laws of thermodynamics to the study of solutions of high-polymeric substances has proved very successful and has permitted a more penetrating study of the processes of solution and of swelling. A thermodynamic investigation of these processes has shown that the change of entropy in the system plays an important role in the solution of polymers, and it has been shown experimentally that the solution of polymers is accompanied by an increase of entropy which is hundreds of times as great as the ideal entropy of the system[1]. Theoretical calculations of the entropy of the system during solution of polymers confirms the experimental data[2].

In view of the observed sharp increase of the entropy of the system, it must be concluded that polymers mix with low-molecular liquids chiefly by diffusion, and this results in a highly irregular distribution of the molecules of the high-molecular and low-molecular components of the solution. The presence of strong forces of attraction between the macromolecules of the polymer and the molecules of the low-molecular liquid must cause a preferential distribution of the molecules in the system and, consequently, a small increase of entropy. In the solution phase, the chains can not be distributed in more different ways than in the polymer phase itself. Despite the large forces of attraction between the polymer chains and the molecules of the solvent, diffusion of the chains in the solution either does not take place at all or comes to a stop. Therefore one can expect that the exothermic swelling of polymers must be limited; in fact, in most cases this limited swelling is accompanied by a considerable evolution of heat.

To determine why polymers are mutually soluble or insoluble, *i.e.*, the reasons why they are compatible or incompatible, it is necessary to calculate the thermodynamic functions of the components and their changes during solution. It is often very important to know the change of heat content of a system during swelling and solution, since the change of heat content indicates a change of intermolecular activity.

The change of the heat content of the system during solution is the integral heat of solution, measured with a calorimeter at constant pressure. The experimental measurement of this parameter for solutions of high polymers is a difficult task, since the processes of swelling and solution continue for a long time. For this reason most investigators have used various theoretical equations for calculating the values of ΔH.

In the present work the integral heats of solution of several synthetic polymers, measured experimentally, are reported.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Colloid Journal* (USSR), Vol. 7, No. 6, pages 474–477 (1950).

EXPERIMENTAL PART

In determining heats of solution, a cylindrical Dewar flask, which served as an ordinary calorimeter, was used. The calorimeter was placed in a water thermostat, the temperature of which was mechanically kept constant in each experiment. All the measurements were made in the temperature range of 24–26° C. The experimental method is not described here, since it has been explained in detail in earlier publications[3]. The following synthetic polymers were investigated: butadiene rubber, butadiene-styrene rubber, polystryene, butadiene-acrylonitrile rubber, polychloroprene, and polyisobutylene.

It should be noted that in every case where the heat effects of the solutions were studied, no relation between the concentration and the integral heat of solution was observed. This is shown by the data in Table 1.

TABLE 1

HEATS OF SOLUTION OF POLYMERS IN BENZENE

	Weight of polymer (g.)	Concentration of polymer (%)	Calorimetric heat (cal. per degree)	ΔT	Q (cal.)	Q (cal. per g.)
Butadiene rubber	3.2212	1.61	114	−0.045	−5.13	−1.59
	3.7014	0.93	204	−0.024	−4.90	−1.32
	0.4390	0.22	128	−0.005	−0.64	−1.46
Butadiene rubber (Buna-S)	15.3738	3.84	183	−0.028	−5.12	−0.33
	10.7748	2.69	199	−0.021	−4.18	−0.39
Polystyrene	5.9620	2.98	98	+0.152	+14.9	+2.49
	1.7126	0.86	99	+0.043	+ 4.3	+2.43
Butadiene-acrylonitrile rubber (Buna-26)	2.3076	0.58	177	−0.018	−3.18	−1.38
	1.9906	0.50	206	−0.014	−2.88	−1.44
Butadiene-acrylonitrile rubber (Buna-40)	3.4030	0.85	173	+0.036	+6.23	+1.83
	3.5058	0.83	198	+0.027	+5.35	+1.52

All the values in Table 1 are mean values, obtained from at least two, and sometimes more, similar experiments. It follows from these results that, within the limits of experimental error, the values of the integral heat of solution are constant for concentrations which differ approximately eight-fold. The absence of any relation between the concentration and the heat of solution proves the liquid structure of all the polymers studied[4].

The mean values of the heats of solution of synthetic polymers in benzene, obtained from the data in Table 1, are given in Table 2.

TABLE 2

HEATS OF SOLUTION OF POLYMERS IN BENZENE

Polymer	Integral heat of solution (calories per gram)
Butadiene rubber (Sample No. 1)	−1.46
Butadiene rubber (Sample No. 2)	−2.57
Polystyrene	+2.46
Butadiene-styrene rubber	−0.36
Butadiene-acrylonitrile rubber (Buna-26)	−1.39
Butadiene-acrylonitrile rubber (Buna-40)	+1.67
Polychloroprene	−0.12

Table 2 shows that both the sign and the magnitude of the heat of solution depend on the chemical constitution of the polymer. First of all, the effect of the addition of atomic groups differing in polarity from the CH_2 groups to the hydrocarbon chain is evident. Thus the presence of carbon in the side chains of the benzene nuclei causes a positive effect (styrene). When the benzene nuclei are located on the hydrocarbon chain, a negative heat effect is observed (butadiene-styrene copolymer).

It is interesting to note that in this particular case the heats are additive. We investigated Buna rubber composed of 75 per cent styrene and 25 per cent butadiene. One gram of this rubber contained 0.75 gram of styrene and 0.25 gram of butadiene. The heat of one gram of this rubber was calculated from the data in Table 2 for polystyrene and butadiene rubber, and the following result was obtained:

$$-.75 \times 1.46 + 0.25 \times 2.46 = -1.095 + 0.615 = -0.38 \text{ calorie per gram.}$$

The value obtained is very close to the heat of solution of butadiene-styrene rubber calculated from the experimental data, *i.e.*, −0.36 calorie per gram.

When a small number of hydrogen atoms is substituted by nitrile groups (26 per cent of acrylonitrile), heat is absorbed during solution, and when a large number of hydrogen atoms is substituted by nitrile groups (40 per cent of acrylonitrile), a positive heat effect is observed during solution.

The sign of the heat of solution is closely related to the mechanical behavior of these polymers. The more elastic polymers, with more flexible chains, absorb heat during solution, whereas the less elastic polymers, with chains of limited flexibility, evolve heat during solution.

Despite the presence of C—Cl groups in polychloroprene, their widely scattered distribution in the chains does not increase the barrier potential of the chain. Consequently the high elastic properties of polychloroprene are preserved. As a polymer possessing flexible chains, polychloroprene dissolves with a large negative heat effect.

Thus we see that heats of solution can provide useful information about the structure of polymers.

Data on two samples of butadiene rubber are given in Table 2. These samples were taken from two factory batches, and their technical behavior differed greatly. Furthermore, according to the data, Sample No. 2 behaved like a material with structure formation. Accordingly it seems that the more negative heat effect of Sample No. 2 is a result of the absorption of more heat during rupture of the cross-linkages.

Similar phenomena were observed during the swelling of several types of polychloroprene. For example, during the swelling of Neoprene which had been aged in our laboratory for about one and one-half years, a very strong absorption of heat, that is, about 8.5 calories per gram, was observed. Such a large absorption of heat is explained by the consumption of heat during the destruction of the crystal lattice formed by crystallization of the Neoprene.

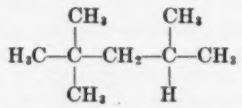
The value of the heat of solution indicates not only the nature of the polymer, but also the nature of the solvent. The heats of solution of polyisobutylene in four different solvents were measured, and the results are shown in Table 3.

TABLE 3

INTEGRAL HEATS OF SOLUTION OF POLYISOBUTYLENE IN FOUR SOLVENTS

Solvent	Benzene	Toluene	n-Heptane	Isooctane
Integral heat of solution in calories per gram	−1.62	−0.44	−0.34	0

It follows from the data in Table 3 that the nature of the solvent has an influence on the integral heat of solution. The polyisobutylene-isooctane system is particularly interesting. The isooctane or 2,2,4-trimethyl pentane used as solvent has the constitution:



that is, it is a hydrogenated dimer of a polyisobutylene chain. In this case it seems that the energy of the reaction between the isobutylene units is equal to the energy of the reaction between one polyisobutylene unit with one molecule of isooctane[5]. Hence, from a theoretical viewpoint, polyisobutylene must dissolve in its own dimer with zero heat effect. This is confirmed by the experimental data. From this it must be concluded that, during solution in isooctane, the barrier potential of the polyisobutylene chain does not change.

CONCLUSIONS

1. The heat of solution of a high polymer depends on the nature of the solvent as well as on the nature of the polymer.
2. The value and sign of the heat of solution of a polymer are related to the structure of the polymer and its mechanical behavior. For polymers which have relatively flexible chains, the heats of solution are negative; for polymers which have relatively rigid chains, the heats of solution are positive.
3. The value and sign of the heat of solution indicate to a certain degree the change of the barrier potential of the polymer chain in any given solvent.

ACKNOWLEDGMENT

In ending we wish to express our gratutude to V. A. Kargin for the interest which he has shown in this investigation.

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RADICAL MECHANISMS IN SATURATED AND OLEFINIC SYSTEMS. II. DISUBSTITUTIVE CARBON–CARBON CROSS-LINKING BY TERTIARY ALKOXY RADICALS IN ISOPRENIC OLEFINS AND RUBBER *

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The efficiency of *tert.*-butoxy radicals in dehydrogenating olefinic and paraffinic hydrocarbons, thereby permitting the coupling of the resulting radicals, has been demonstrated. The process provides a ready means for cross-linking carbon chains by carbon-to-carbon bonds; moreover, by repetition of the process in long chains, an increasing degree of cross-linking can be obtained. It is of considerable practical interest to observe the effect on the physical properties of long-chain hydrocarbons (and especially of polyisoprenic and polybutadienic rubbers) of increasing gradually the proportion of carbon-carbon cross-links per molecule for ultimate comparison with corresponding effects in the sulfur-bridge cross-linking of the same chains, which, so far as is known, is mainly of substitutive-additive type, the bridges containing 1–6 sulfur atoms. The present account deals principally with the cross-linking of natural rubber molecules by radicals, but briefly reports also a series of preliminary experiments carried out with short-chain olefins ("model" rubber molecules) containing 1,4-isoprene units. For comparison with rubber, it was desirable to have all the isoprene units of the model molecules of the unmodified rubber-type, $-\overset{\alpha}{C}H_2-\overset{\beta}{C}Me=\overset{\gamma}{C}H-\overset{\delta}{C}H_2-$, which, because of the primary character of the methylic C—H bonds, would not be liable to undergo any very appreciable degree of attack at other than the two secondary α-methylene groups. But obviously this was only partly feasible, since all the terminal isoprene units of relatively short-chain polyisoprenes necessarily have their outermost α-methylene groups embodied in primary methyl groups, thus making the comparison with rubber not quite exact in respect of the distribution of radical attack. It is particularly to be noted that the two isoprene units of the most readily available model molecule, dihydromyrcene or, better, its synthetic counterpart, 2,6-dimethylocta-2,6-diene, which does not contain the occasional vinylic isoprene units, $CH_2:CMe\cdot CH_2\cdot CH_2$, to which naturally occurring terpenic chains are liable, each contain only one secondary α-methylene group; hence attack on the molecule by radicals, provided that not more than one radical per unit is employed, is likely to be almost wholly confined to the mid-chain pair of methylene groups. To ensure that every *tert.*-butoxy radical may have a good chance of encountering an unattacked isoprene unit, the initial concentration of the former has been restricted to an average of one per

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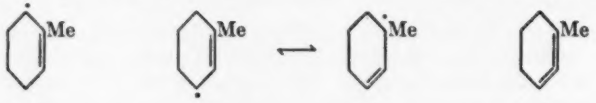
two isoprene units in the case of monoisoprenes, and to one per three units in that of di- and tetraisoprenes. Hence, the maximum average degree of cross-linking which can ensue falls far short of one cross-link emanating from every unit of every chain. The monoolefins selected for examination are two disubstituted isoprenes, $R \cdot CH_2 \cdot CMe{:}CH \cdot CH_2R'$, in the first of which the groups R and R′ are polarly equal (since they consist of the same system $\cdot CH_2 \cdot CH_2 \cdot$), and in the second are polarly unequal, so that the distribution of negative activation[1] within the isoprenic system may be considered normal in the first and somewhat unbalanced in favor of C_δ in the second.

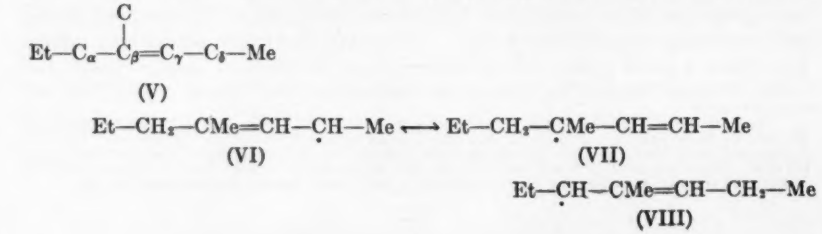
The cross-linking of 1-methylcyclohexene and of 4-methylhept-3-ene.—Dehydrogenation of the two secondary α-methylenic groups in 1-methyl*cyclo*hexene can give only the radical forms (I–III), since the amount of attack at the methyl group (as experience in such cases confirms) is likely to be negligible.



(I) (II) (III) (IV)

Of these three, two are resonance forms of the mesomeric radical (IV). By coupling the three forms in pairs, a maximum of six structurally different dimers becomes possible, and by further coupling of the original and the new radical forms, still larger numbers of isomeric trimers and isomeric higher polymers are likely to arise. In practice, fractions consisting of dimers ($C_{14}H_{22}$, $\overline{2}$), trimers ($C_{21}H_{32}$, $\overline{3}$), tetramers ($C_{28}H_{42}$, $\overline{4}$), and higher polymers[2] were readily separated in relative proportions of about 5:2:1:2. The individual isomers constituting the dimer could not be separated by distillation or by fractionation of their tetrahydrides or tetrabromides; and, in view of the rather complicated character of the degradative scission products to be expected, no detailed analysis of structural forms was attempted.

The polar inequality between the ethyl and methyl groups in 4-methylhept-3-ene may be expected to enhance slightly the negative activation at C_δ (V) relative to that in an ordinary rubber unit, in which the flanking alkenylmethyl groups, RR′, although different in size and detail, may be considered polarly equal. This should cause a somewhat increased degree of substitutivity at C_δ, and, of course, at the corresponding resonance position C_β. By treatment of the olefin with the peroxide, the usual mixture of dimers and higher polymers was obtained. The dimer fraction ($C_{16}H_{30}$, $\overline{2}$) was composed of a mixture of hexadecadienes, which was shown by infrared spectrographic examination to contain olefinic groupings of the type, RR′C:CHR″, characterizing the original olefin and its derived radicals (VI and VIII)[3], as well as of a new type, RCH:CHR, doubtless resulting from incorporation in the dimers of the resonance form (VII). The proportion of the new grouping, as deduced from the relevant



extinction coefficient, was computed to be about 15 per cent, which value is at least equal to that found for comparable (resonance-sited) C_β-substitution in 2-methylbut-2-ene[4]. It was of interest that the recovered monomeric olefin gave evidence of containing traces of unsaturation of the type $\cdot CH{:}CH\cdot$, which must be attributed to hydrogen transfer reactions having occurred, *inter alia*, between the tertiary methylheptenyl radicals (VII) and the original olefin molecules:

$$CH_2Et—\dot{C}Me—CH{=}CHMe + CH_2Et—CMe{=}CH—CH_2Me \longrightarrow$$
$$CH_2Et—CHMe—CH{=}CHMe + CH_2Et—CMe{=}CH—\dot{C}HMe$$

The cross-linking of 2,6-dimethylocta-2,6-diene and of digeranyl.—The dimers, trimers, etc., obtained from the first (diisoprenic) olefin could not be satisfactorily separated by distillation, owing to their high boiling point: hence, the presence of more than one cross-link connecting a pair of molecules could not easily be ascertained. The polymer mixture, when freed from unchanged monomer, proved to contain olefinic groupings of the original type, $RR'C{:}CHR''$, as well as an appreciable proportion of the type $R\cdot CH{:}CHR'$, and even some of the type $RR'C{:}CH_2$. This result was to be expected, but the additional observation that the polymer mixture showed only 82 per cent of the original olefinic unsaturation had not been foreseen. The loss of unsaturation could only have been due to partial cyclization, and the appearance of the latter in this example must apparently be deemed to result from the carbon chain now being of suitable length, unsaturation-pattern, and negative activation at one end of the double bond for intramolecular radical-double bond additions to succeed, for example:

$$\dot{C}Me_2—CH{=}CH—CH_2—CMe{=}CH\cdot CH_3$$
$$\longrightarrow CMe_2—CH{=}CH—CH_2—\dot{C}Me—CHMe.$$

The second (tetraisoprenic) olefin $H[CH_2\cdot CMe{:}CH\cdot CH_2]_2\cdot[CH_2\cdot CH{:}CMe\cdot CH_2]_2H$ contained, in the main, two ordinary isoprenic units (these being arranged in tail-to-tail fashion)[5], and two possessing only one secondary α-methylene group each. In spite of the above-mentioned deficiency of reagent employed (one *tert.*-butoxy-radical per three units), one-fifth of the olefin molecules taken remained unlinked, so that (on average) only about 0.8 cross-link per digeranyl molecule could have been formed. In the process, just over three-quarters of the digeranyl molecules had become converted into tetrameric aggregates by cross-linking, so within these tetramer molecules most of the pairs of digeranyl chains were joined (on average) only by one cross-link, although occasional pairs (about 2 per 5 tetramers) were joined by two. Some reduction in the original degree of unsaturation occurred in these polymers also, and this again must be attributed to the occurrence of a minor degree of additive (radical to double bond) cyclization.

The cross-linking of rubber.—In the case of rubber, with its average of about 5000 isoprene units per molecule, observations of cross-linking were made at 100° and at 140° with raw (smooth smoked sheet) and acetone-extracted samples, varying proportions of di-*tert.*-butyl peroxide being used as reagent. The specimens became progressively insoluble in benzene and other solvents

TABLE I

REACTION OF RAW RUBBER WITH DI-TERT.-BUTYL PEROXIDE (6 HOURS AT 140°)

Peroxide (g. per 100 g. of rubber)	Q_m	$10^3 M_c$	Tensile strength (kg. cm.$^{-2}$)	Elongation at break (%)	Modulus (kg. cm.$^{-2}$) 100%	300%	500%	700%
0	—	—	54	925	3.1	3.6	4.9	18
1.45	4.4	7.5	141	645	5.4	13	29	—
2.1	3.9	6.1	145	580	7.4	18	60	—
2.5	3.7	5.7	162	570	6.2	20	82	—
2.9	3.4	4.7	178	555	11	22	93	—
3.4	2.6	3.1	123	470	8.2	25	—	—
5.4	2.2	2.3	29.5	250	13	—	—	—
7.65	2.1	2.2	16	85	—	—	—	—
10.1	1.3	1.0	12	40	—	—	—	—
15.7	1.0	0.85	12	20	—	—	—	—

and showed mechanical properties and swelling characteristics indicating the progressive occurrence of vulcanization. Determination of the equilibrium swelling constant[6] (Q_m) of the vulcanized specimens immediately after their preparation permitted an estimate to be made of the average molecular weight between junction points (M_c) in the cross-linked chains, the latter value being inversely proportional to the number of new cross-links formed[7].

The numerical results obtained for the physical characteristics of the cross-linked samples are given in Tables I and II. These demonstrate very clearly that di-*tert.*-butyl peroxide is highly effective in producing good rubber vulcanizates, and the physical nature of the samples indicates that uniform vulcanization has been effected. The values of Q_m and M_c steadily decrease with increasing peroxide concentration, thereby indicating a progressive increase in the degree of cross-linking.

The figure shows the effect of peroxide concentration on the tensile strengths of the samples. The two curves show the characteristic features of well defined maxima, the tensile strengths increasing with increasing amounts of peroxide up to a certain critical peroxide concentration, beyond which they fall very sharply[8]. The effect of the removal of nonrubber components (resin

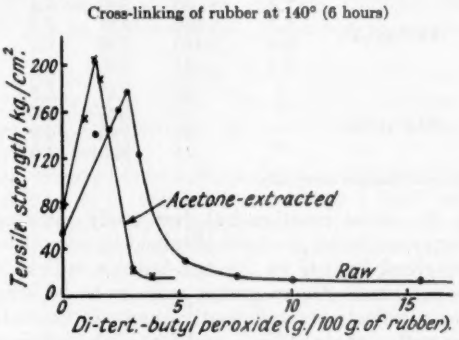
TABLE II

REACTION OF ACETONE-EXTRACTED RUBBER WITH DI-TERT.-BUTYL PEROXIDE

Peroxide (g. per 100 g. of rubber)	Reaction conditions: Hrs.	Temp.	Q_m	$10^3 M_c$	Tensile strength (kg. cm.$^{-2}$)	Elongation at break (%)	Modulus (kg. cm.$^{-2}$) 100%	300%	500%	700%
0	—	—	—	—	80	900	3.3	5.7	11	34
1.0	6	140°	4.3	7.4	155	705	7.3	14	32	154
1.45			4.1	6.8	206	660	6.5	16	56	—
1.7			4.1	6.8	190	625	6.6	17	64	—
3.1			2.6	3.0	22	210	12	—	—	—
3.95			2.1	2.2	16	100	16	—	—	—
51.5			0.74	0.44	—	—	—	—	—	—
2.4	24	99.5°±0.5°	8.7	—	109	905	—	6.7	14	43
3.0			8.0	—	>95	835	—	6.9	14	46
3.5			7.2	—	>116	875	—	6.6	15	49
4.5			6.6	—	148	890	—	6.7	16	55
5.0			6.2	—	>137	865	—	6.9	16	55
3.0	72	99.5°±0.5°	5.5	—	184	815	—	11	30	104
3.55			6.0	—	172	820	—	9.4	26	90

acids, antioxidants, *etc.*) from the rubber by acetone extraction is to increase the maximum attainable tensile strength and also to reduce the peroxide concentration required to produce this maximum figure. For instance, raw smoked sheet requires about 2.9 per cent of peroxide to give a maximum tensile strength of 178 kg. cm.$^{-2}$, whereas acetone-extracted smoked sheet gives a vulcanizate with a maximum tensile strength of 206 kg. cm.$^{-2}$ with only 1.45 per cent of peroxide. The nonrubber components presumably compete with the polyisoprene chains for interaction with the peroxide, and so diminish the efficiency of the peroxide as a cross-linking agent.

As the peroxide concentration increases beyond a certain optimum value, the desirable properties of the vulcanizates (good tensile strength and elasticity) deteriorate; and with peroxide concentrations of about 5–16 per cent, the samples show a substantial loss of rubberlike properties, displaying brittleness, low tensile strength, and negligible elasticity. The results thus demonstrate that cross-linking of rubber chains must be restricted within very narrow limits to give useful products.



The increase in oxygen content of the peroxide-vulcanized samples was only very small (0.34–0.355 per cent), as based on direct oxygen determination[9], for much of the peroxide was converted into a mixture of *tert.*-butanol and acetone: in one rather extreme case investigated [peroxide equal to 48.2 per cent (w/w) of the rubber; 6 hours' heating], these represented (respectively) 41.1 and 36.6 per cent of the peroxide taken. Thus the major and probably the sole olefinic reaction in the peroxide vulcanization of rubber is still dehydro cross-linking, producing ultimately a three-dimensional net structure in which all the cross-links are C—C bonds. Decomposition of some of the *tert.*-butoxy-radicals to yield acetone simultaneously gives methyl radicals ($Me_3C—O\cdot \rightarrow Me_2CO + Me\cdot$), a part of which may dimerize without any cross-linking effect, and the remainder participate in the dehydrogenation which precedes cross-linking ($RH + Me\cdot \rightarrow MeH + R\cdot$; $R\cdot + R\cdot \rightarrow R—R$, where R is an isoprene unit of a rubber chain). The likelihood, however, of a portion of the dehydrogenating capacity being lost through acetone-formation becomes less as the peroxide concentration decreases, and is probably insignificant up to the optimum concentration value of the rubber. The scanty incorporation of *tert.*-butoxy radicals in the rubber, as indicated by the low oxygen content, is in sharp contrast to the heavy incorporation of the more electrophilic benzoyloxy radicals in the corresponding treatment of rubber with dibenzoyl peroxide[10]; moreover, the contrast corresponds to a notable difference between the two

peroxidic reagents, since the extensive and wasteful formation of ester characterizing the benzoyl compound has no counterpart (ether formation) in the case of the alkyl compound.

It was attractive to investigate whether, by use of a rather more energetic alkoxy radical than the *tert.*-butyl compound, superior peroxide-vulcanizates could be obtained from natural rubber by operating at temperatures well below the usual reaction temperature of 140°. To this end the ethoxy radical, derived by thermal decomposition of diethyl peroxide, was employed. The relevant physical properties of the cross-linked rubbers obtained at 140° and at about 100° are given in Table III. These, however, reveal that no advantage

TABLE III

REACTION OF ACETONE-EXTRACTED RUBBER WITH DIETHYL PEROXIDE

Peroxide (g. per 100 g. of rubber)	Reaction conditions			Tensile strength (kg. cm.$^{-2}$)	Elongation at break (%)	Modulus (kg. cm.$^{-2}$)		
	Hrs.	Temp.	Q_m			300%	500%	700%
1.2	6	140°±0.5°	7.0	> 90	830	6.6	13	43
1.5			6.7	>102	830	7.6	14	53
2.8			5.4	>116	790	8.9	20	69
3.7			5.1	161	825	9.8	19	82
0.94	6	99.5°±0.5°	*	36	835	5.7	7.6	21
1.9			*	34	825	5.0	7.0	18
2.7			*	33	780	4.9	7.8	23
3.6			*	41	825	4.0	8.0	23

* Q_m values too high to be obtained accurately.

accrues by using the more reactive but less easily manipulated peroxide. Whether or not the cross-linked products obtained by use of the ethoxy radical resemble those obtained by use of the *tert.*-butoxy radical in being almost entirely free from combined ethoxy groups remains to be investigated. It is possible that ethoxy radicals are sufficiently energetic (unstabilized) to unite reasonably rapidly with olefinic radicals and (or) with olefinic double bonds to ensure that a substantial degree of wasteful and deleterious ethoxylation of the vulcanizate occurs: $RH \xrightarrow{-H\cdot} R\cdot \xrightarrow{\cdot OEt} R{-}OEt$; $-C{=}C- + \cdot OEt \rightarrow -\dot{C}-C(OEt)-$. Also it seems probable that a greater degree of thermal decomposition of the ethoxy radical occurs ($CH_3{-}CH_2{-}O\cdot \rightarrow CH_3\cdot + H{-}CHO$) than is the case with the *tert.*-butoxy radical.

EXPERIMENTAL

(Microanalyses by W. T. Chambers, (Miss) E. Farquhar, and (Mrs.) H. Hughes. Spectrographic observations by H. P. Koch.)

Cross-linking of 1-methylcyclohexene.—The methylcyclohexene (50 g., 0.5 mol.; b. p. 109–110°/760 mm., $n_D^{19.5}$ 1.4503) and di-*tert.*-butyl peroxide (18.25 g., 0.125 mol.) were heated in a Carius tube sealed under nitrogen, at 140° for 24 hours. The product (66.0 g.), a colorless mobile liquid, gave on distillation the fractions: (1) b. p. 82–110° (44.2 g.); (2) b. p. <86°/1 mm. (0.35 g.); (3) b. p. 86–94°/1 mm. (10.15 g.); (4) b. p. 94–146°/1 mm. (0.45 g.); (5) b. p. 146–149°/1 mm. (3.85 g.); (6) b. p. 203–204.5°/1 mm. (2.4 g.); (7) a colorless, glasslike residue in the still (about 4.0 g.) which was not further investigated. Fraction (1) gave on aqueous extraction, 18.0 g. of water-soluble compounds, which consisted mainly of *tert.*-butanol (isolated as described in earlier[11]), b. p. 82–82.5°/760 mm.; only traces of acetone were present, these being identified

and determined as the 2,4-dinitrophenylhydrazone, m. p. 124–125° (yield 0.1 g., equiv. to 0.027 g. of acetone). The nonaqueous layer was unchanged methylcyclohexene (25.0 g.) which, after being dried ($CaCl_2$) and distilled over sodium, had b. p. 109–110°/760 mm., $n_D^{1.75}$ 1.4510.

Fraction (3), a colorless oily liquid, was identified as *dimethyldicyclohexenyl*. Though molecularly homogeneous, it doubtless consisted of a mixture of structural isomers. Redistillation over sodium, in nitrogen, gave a main fraction, b. p. 74–78°/0.5 mm., n_D^{20} 1.5116. [Found, for two different samples: C, 88.35, 88.55; H, 11.80, 11.65%; *M* (micro-Rast), 214, *M* (benzene), 233. $C_{14}H_{22}$ requires C, 88.35; H, 11.65%; *M*, 190.] This olefinic dimer absorbed hydrogen (Adams catalyst) equivalent to 2.0 double bonds per mol. A larger portion (1.37 g.) in absolute ethanol (150 cc.), when hydrogenated over palladium-charcoal (200 mg.), absorbed 305.0 cc. of gas at N.T.P. (Calc.: 322.9 c.c.) to give the tetrahydride, dimethyldicyclohexyl. This, when distilled over sodium, gave two fractions: (1) b. p. 64–68.0°/0.5 mm., n_D^{20} 1.4827 (0.56 g.). (Found: C, 86.7; H, 13.45%); and (2) b. p. 68.0°/0.5 mm., n_D^{20} 1.4831 (0.47 g.). (Found: C, 86.6; H, 13.5. Calc. for $C_{14}H_{26}$: C, 86.5; H, 13.5%.) Both fractions were colorless mobile liquids, stable towards potassium permanganate solution and towards bromine.

Treatment of the dimeric olefin (in chloroform) at 0° with bromine led to the absorption of 2.0 mols. of halogen. The product, however, on removal of the solvent rapidly evolved hydrogen bromide and darkened; no solid tetrabromides could be isolated.

The colorless, viscous liquid forming fraction (5) was redistilled over sodium in nitrogen. It had b. p. 144–148°/1 mm., n_D^{20} 1.5339, and gave analytical values corresponding to *trimethyltercyclohexenyl*. [Found: C, 88.75, 88.8; H, 11.25, 11.35%; *M* (in benzene), 268, 280, 300; unsaturation value (catalytic hydrogenation), $\overline{2}.87$. $C_{21}H_{32}$ requires C, 88.65; H, 11.35%; *M*, 284, $\overline{3}$.] This triolefinic trimer fraction probably contained a number of structural isomers.

Fraction (6) was an extremely viscous, colorless semiglass, which, on distillation over sodium, gave a small fraction, b. p. <186°/0.1 mm., and a main fraction, b. p. 186–192°/0.1 mm., the latter doubtless consisting of the *tetramer*. (Found: C, 89.0; H, 11.35. $C_{28}H_{42}$ requires C, 88.8; H, 11.2%.)

Cross-linking of 4-methylhept-3-ene.—The olefin, prepared by dehydration of 4-methylheptan-4-ol (b. p. 70–78°/20–23 mm., n_D^{20} 1.4258) with about 0.5% of iodine, had b. p. 116–117.0°/738 mm., n_D^{20} 1.4175; infrared spectrographic analysis indicated its main type of unsaturation to be of trialkylethylene type, $R \cdot CH{:}CR'R''$, but there was also a small amount of the *as*-dialkylethylene type $RR'C{:}CH_2$ present, indicative of the 4-methyleneheptane isomer. Other types of unsaturation were definitely absent.

A mixture of the olefin (112 g.; 4 mols.) and the peroxide (36.5 g.; 1 mol.) was heated at 140° for 24 hours in nitrogen-filled Carius tubes. The colorless liquid product (148.0 g.) gave on distillation the fractions: (1) b. p. 80–120°/742 mm. (89.3 g.), (2) b. p. <28°/21 mm., n_D^{20} 1.4187 (8.9 g.), and (3) a liquid residue, n_D^{20} 1.4641 (47.9 g., equiv. to 42.7% of the original olefin), consisting entirely of olefinic hydrocarbon components (Found: C, 86.35, 86.1; H, 13.65, 13.65%.) A portion (46.8 g.) of fraction (3) gave on redistillation in nitrogen the following fractions: (4) b. p. <71°/0.05 mm., n_D^{20} 1.4510 (2.0 g.); (5) b. p. 67°/0.01 mm.—72°/0.05 mm., n_D^{20} 1.4586 (25.3 g.), and a residue (6), n_D^{20} 1.4775 (19.0 g.). (Found: C, 86.15; H, 13.4%), which was not further investigated.

Fraction (1) gave on extraction with water (300 g. + 200 g.) a mixture of water-soluble components (36.0 g.). Treatment of the extract with 2,4-dinitrophenylhydrazine solution (in 2*N* hydrochloric acid) gave acetone 2,4-dinitrophenylhydrazone (0.32 g., equiv. to 0.08 g. of acetone). The only other water-soluble material was *tert.*-butanol (about 36.0 g., equiv. to 97.3% of the peroxide employed).

The olefin present in fractions (1) and (2) was combined and redistilled (in nitrogen) over sodium. It gave a monomeric fraction, b. p. 117.0–120.0°/755 mm., n_D^{20} 1.4184.

Fraction (5), a colorless oily liquid, was obviously the dimer, *hexadecadiene*. [Found: C, 86.1; H, 13.6%; *M* (in benzene), 246. $C_{16}H_{30}$ requires C, 86.4; H, 13.6%; *M*, 222.] A portion of the redistilled dimer (3.1 g.), dissolved in absolute ethanol (50 cc.), absorbed over palladium-charcoal (1.0 g.) at room temperature and pressure 535 cc. (N.T.P.) of hydrogen, *i.e.*, 85.6% of the theoretical amount. The hexadecane so obtained was a colorless liquid, b. p. 64–67°/0.1 mm., n_D^{20} 1.4439 (2.3 g.). (Found: C, 84.9; H, 14.95. Calc. for $C_{16}H_{34}$: C, 84.85; H, 15.15%.) The product was stable towards aqueous potassium permanganate for a long time.

Infrared spectrographic examination of the recovered methylheptene revealed a higher ratio of $CH_2{:}CRR'$ to $R{\cdot}CH{:}CR'R''$ than existed in the original olefin, and also showed a band at 963 cm.$^{-1}$ consistent with the presence of a trace of $R{\cdot}CH{:}CHR'$, which was absent from the original olefin. In the methylheptene dimer the ratio of $CH_2{:}CRR'$ to $R{\cdot}CH{:}CR'R''$ was about the same as in the original olefin. The appearance of a strong new band at 975 cm.$^{-1}$ and the broadening at the olefinic absorption band at 1640 cm.$^{-1}$ are attributed to a new form of unsaturation, $RR'R''C{\cdot}CH{:}CHR'''$, not present in the original olefin. In the fully-hydrogenated methylheptene dimer the olefinic absorption in the 1650 cm.$^{-1}$ region and the strong bands at 847 cm.$^{-1}$ and 9.75 cm.$^{-1}$, assigned to $R{\cdot}CH{:}CR'R''$ and $R{\cdot}CH{:}CHR'$, respectively, were all absent.

Cross-linking of 2,6-dimethylocta-2,6-diene.—The olefin, b. p. 56°/14 mm., n_D^{20} 1.4490 (13.8 g.; 3 mols.), was heated with the peroxide (4.9 g., 1 mol.) in a nitrogen-filled Carius tube at 140° for 24 hours. Distillation of the product (18.5 g.) gave *tert.*-butanol, together with unchanged olefin, leaving an olefinic polymer residue (6.9 g., equiv. to 50% of olefin taken), having n_D^{24} 1.4945. [Found: C, 87.3; H, 12.45%; *M* (in benzene), 362, 372.] Microhydrogenation of the polymer indicated a considerable reduction in unsaturation. (Found: $\overline{|}_{1.63}$ to $\overline{|}_{1.65}$ per C_{10} unit.) Infrared spectrographic examination of the polymer indicated, in addition to the original type of unsaturation, appreciable amounts of $RR'C{:}CH_2$ and $R{\cdot}CH{:}CHR'$ double-bond structures.

Cross-linking of digeranyl.—The olefin[12] had b. p. 181.0–181.3°/13.5 mm., n_D^{20} 1.4831. (Found: C, 87.7; H, 12.65%; $\overline{|}_{4.05}$. Calc. for $C_{20}H_{34}$: C, 87.5; H, 12.5%; $\overline{|}_4$.) A mixture of the olefin (8.22 g.; 1.5 mol.) and the peroxide (2.92 g., 1 mol.) was sealed in a Carius tube under 0.01 mm. of nitrogen, and heated at 140° for 24 hours. The product was transferred to a horizontal pot still with a water-cooled condensing finger. Evaporative distillation at <0.01 mm. gave, first, volatile products, and then the following fractions: (1) at 50–53°, consisting mainly of digeranyl, n_D^{20} 1.4850 (1.61 g.; equiv. to 19.6% of olefin taken). [Found: C, 87.4; H, 12.6%; *M* (in benzene), 279, 295]; (2) at 53°, a liquid, $n_D^{20.2}$ 1.4859 (0.115 g.; equiv. to 1.4% of olefin taken); (3) a colorless very viscous residue, n_D^{20} 1.5168 (6.40 g.; equiv. to 77.85% of olefin taken) [Found: C, 87.75; H, 12.1%; M (in benzene), 985, 990]. Microhydrogenation of

fraction (3) showed that it contained about 72%. (Found: 71.6, 72.1%) of the unsaturation of the original digeranyl. The results of infrared analysis of fraction (3) were similar to those for the dimethyloctadiene residue given above.

Cross-linking of natural rubber with di-tert.-butyl and diethyl peroxide.—The former peroxide, prepared according to Milas and Surgenor[13] had b. p. 109.0–110.0°/760 mm., n_D^{20} 1.3882 (Found: C, 65.7; H, 12.3. Calc. for $C_8H_{18}O_2$: C, 65.7; H, 12.4%). The diethyl peroxide, prepared by Wiley's method[14] had b. p. 62.5–63.5°/759.5 mm., $n_D^{16.1}$ 1.3711, $n_D^{20.5}$ 1.3690. (Found: C, 53.15; H, 11.25. Calc. for $C_4H_{10}O_2$: C, 53.3; H, 11.2%.) Harris and Egerton[15] give b. p. 58–59°/625 mm., $n_D^{16.5}$ 1.3715, and Wiley[14] gives b. p. 61–65°, n_D^{23} 1.3700.

The rubber hydrocarbon used was a sample of smooth smoked sheet rubber. The acetone-extracted sample was prepared by extracting strips of the rubber in a nitrogen atmosphere for 24 hours, followed by drying of the swollen strip in vacuo for 3–5 days at 10^{-5} mm.

The experimental technique generally used was as follows. Strips of the rubber (about 4 × 0.5 × 0.1 inch) of known weights were left in contact with the calculated amounts of the appropriate peroxide in tubes sealed in an atmosphere of purified nitrogen. After 24–28 hours' contact, it was assumed that even distribution of the peroxide in the rubber had been attained. The samples were quickly weighed and, while cooled in liquid air to prevent loss of peroxide, were sealed in Carius tubes in a nitrogen atmosphere of about 0.05 mm. pressure and then heated for the appropriate time (6–72 hours) and at the appropriate temperature (99.5° ± 0.5°, or 140° ± 0.5°).

The mechanical properties and equilibrium swelling constants (Q_m) in benzene[7] of all the samples were measured immediately after reaction. These data are given in Tables I–III.

The volatile byproducts obtained in the reaction between di-*tert.*-butyl peroxide and rubber were examined as follows.

Method 1.—A sample of acetone-extracted rubber was dried for 4 days at 10^{-5} mm. and then immediately analyzed. (Found: C, 86.3; H, 11.45; O (direct determination), 0.98, 0.965; ash, 0.25%.) This sample was heated with di-*tert.*-butyl peroxide (51.5 g. per 100 g. of rubber) for 6 hours at 140°. The liquid which separated from the product was shown to be mainly *tert.*-butanol, together with some acetone, but no peroxide. The rubber derivative (a hard brittle solid having no rubberlike properties) was acetone-extracted and dried for 7–9 days at 10^{-5} mm. (Found: C, 87.3, 86.6; H, 11.3, 11.55; O (direct determination), 1.32, 1.32; ash, 0.95%.)

Method 2.—A sample of rubber (17.0 g.), as in (1), was allowed to imbibe the peroxide (8.2 g.) in an atmosphere of nitrogen during 2 weeks, the resulting mixture than being heated under nitrogen for 6 hours at 140°. The liquid product (5.8 g.), which separated out after the reaction, was pumped off at 1 mm. pressure and condensed in a liquid-air trap. It was a colorless liquid boiling entirely over the range 56–80° and was shown to consist of a mixture of acetone (36.6% or peroxide taken), determined and identified as its 2:4-dinitrophenylhydrazone, m. p. 124–125° (mixed m. p. 125°), and *tert.*-butanol (equiv. to 41.1% of peroxide taken), identified as its phenylurethane, n. p. and mixed m. p. 136°. No unchanged peroxide was found.

SUMMARY

The high degree of dehydrogenation effected by *tert.*-butoxy radicals at the α-methylenic groups of olefins enables these radicals to be used for the carbon-to-carbon cross-linking of unsaturated carbon chains, and especially of the

polyisoprenic chains of natural rubber. Such cross-linking amounts to a vulcanization process in which the connecting links between chain molecules are just C—C bonds, which may be expected to have appropriate attributes.

An examination has first been made of the cross-linking produced by *tert.*-butoxy radicals (from di-*tert.*-butyl peroxide) at 140° between the short isoprenic chains in 1-methylcyclohexene, 4-methylhept-3-ene, 2,6-dimethylocta-2, 6-diene, and digeranyl. Cross-linking proceeds efficiently in each case, and the points of union in these isoprene units which become directly joined are not confined to original α-methylenic carbon atoms. Where the reagent radicals are in considerable deficit, *e.g.*, one per two or three of the isoprene units present, those olefin molecules which are attacked become linked together mostly by single unions to form aggregates containing two, three or four molecules; but in the tetraisoprenic olefins the extent to which more than one union is formed between some of the directly linked molecules becomes appreciable.

In natural rubber, cross-linking occurs smoothly and to nearly the full extent corresponding to the (in practice restricted) proportion of peroxidic reagent employed. Good vulcanizates can be so obtained in which the tensile stength is found to increase towards a maximum and then to decline rapidly as the degree of cross-linking steadily increases. Thus to obtain vulcanizates of the optimum physical characteristics, the degree of cross-linking must be suitably chosen. The role of the peroxidic reagent is almost entirely non-additive and non-degradative.

REFERENCES

[1] The method of degradative analysis adopted elsewhere (see Parts V and VII) is unsuitable for examining in detail the effect of altering the negativization balance in favor of C_α or C_β by using in turn different electron-donating substituents R and R'. Doubtless a study of the rates of substitutive (radical) reaction in the differently substituted olefinic chains, as in maleinization, oxidation, and sulfuration, would be more effective.

[2] Actually all dehydropolymers (see Farmer and Moore, *J. Chem. Soc.* **1951**, p. 131).

[3] A proportion of the dimers contained, as expected, groupings of the type $H_2C{:}CRR'$, since the olefin was prepared by dehydration of CHMePr·OH, and so contained a little of the difficulty removable vinylic isomer, $H_2C{:}CPr_2$.

[4] Farmer and Moore, *J. Chem. Soc.* **1951**, p. 149.

[5] The digeranyl employed contained a minor proportion of isodigeranyl, in which one of the isoprenic units is modified (private communication).

[6] Q_m is defined as the volume of solvent (benzene) imbibed at equilibrium swelling by unit volume of rubber.

[7] Gee, *J. Polymer Sci.* **2**, 451 (1947).

[8] The same phenomenon is observed with rubber-sulfur vulcanizates (see Gee, *J. Polymer Sci.* **2**, 451 (1947)).

[9] Chambers, *Proc. 2nd Rubber Technol. Conf. London*, **1948**.

[10] Van Rossem et al., *Kautschuk* **7**, 202, 220 (1931); Farmer and Michael, *J. Chem. Soc.* **1942**, p. 513.

[11] Farmer and Moore, *J. Chem. Soc.* **1951**, p. 131.

[12] The olefin was kindly supplied by D. Barnard.

[13] Milas and Surgenor, *J. Am. Chem. Soc.* **68**, 205 (1946).

[14] Wiley, U. S. patent 2,357,298 (1944).

[15] Harris and Egerton, *Proc. Roy. Soc.* (London) **168A**, 1 (1938).

DYNAMIC STUDY OF REINFORCEMENT *

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The reinforcement of rubber, next to vulcanization, is the most important process on which the development of the use of rubber has been based. Without reinforcement, our tires would indeed be mere shadows of those which we enjoy at present.

In spite of this importance, little is known about the mechanism of reinforcement. For many years it has been recognized that the surface forces (or bond) between rubber and reinforcing filler are the basis of this effect, but more recently consideration has been given to a wider field of the forces of interaction, namely, those between carbon particles as well as those between rubber molecules. It is these forces which give rise to "structure" in rubber compounds. These structures can be modified, destroyed, or even rebuilt, by movements of the "particles" (which from considerations of thixotropy we can regard as clusters rather than individual particles) induced by mechanical movement and (or) heat. It follows, therefore, that if we study the effect of disturbances on the mechanical and electrical properties of a rubber compound, we may be able to throw some light on these diverse structures. The particles upon which the mechanical properties of rubber are based are probably macroclusters and not molecules or individual carbon particles, although the ultimate molecule and individual carbon particle may, and probably do, play a great part in the behavior of the cluster. For the breaking down of random clusters one is concerned with van der Waals forces, and these effects should not, therefore, be confused with the rupture of chemical bonds, such as takes place during the breaking down of the rubber molecule by chemical means. That is an additive effect, as is also the stitching together of rubber molecules by cross-linking, and attempts have been made in this work to avoid conditions which would induce marked chemical deterioration or continued vulcanization.

The conclusions from statistical theory, assuming no interaction forces, predict that the equilibrium modulus of a rubber increases with temperature. In practice this has been found to be true only over a limited range and under circumstances where the forces of interaction are known to be small, *e.g.*, gum stocks and elevated temperatures. Part of the discrepancy between theory and practice can be attributed to the nonequilibrium conditions which tend to prevail in rubber testing. Nevertheless the observed reversal under dynamic conditions of the predicted direction of variation of modulus with temperature suggests that other factors, particularly the existence of interaction forces, are equally, if not more, important. With this viewpoint it is reasonable to use the experimental variation of modulus with temperature as a measure of these interaction forces. For the dynamic mechanical study therefore, the property of dynamic modulus has been selected as a measure of the development of these forces. Furthermore, dynamic modulus has the advantage of being a single measurement from a physical standpoint and is insensitive to frequency under the conditions of test.

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For the dynamic electrical study the property of electrical resistivity under vibration has been employed.

The experimental work was carried out on six mixings, four of which were tire-tread compositions based on natural rubber, Neoprene, Perbunan, and GR-S compounded with a channel black. The remaining two were a similar stock based on natural rubber compounded with a high-modulus furnace black and a natural rubber gum stock for comparison and contrast. The immediate aim was to measure the dynamic modulus of these compositions over a temperature range, in order to get a measure of the type and magnitude of the forces involved when these materials are repeatedly stressed at frequencies comparable with those occurring in service.

The measurement of electrical conductivity under vibration would indicate the rupture or building up of carbon-carbon particle chains as the resistivity increased or decreased.

The most recent views on the theory of fatigue[1] in materials attribute breakdown to the cumulative rupture of cohesive bonds in the material, a process which is initiated at the very first cycle of distortion.

Healing as well as rupture of these weak bonds is a process which is going on all the time, and the predominance of one or the other factor determines the progress of fatigue. The time factors involved in stressing and rest periods must be related to the relaxation of the structure produced in the material with each successive cycle of distortion.

EXPERIMENTAL METHOD

The dynamic properties of rubberlike materials have been measured by various methods[2], and the whole matter was discussed at a recent conference[3].

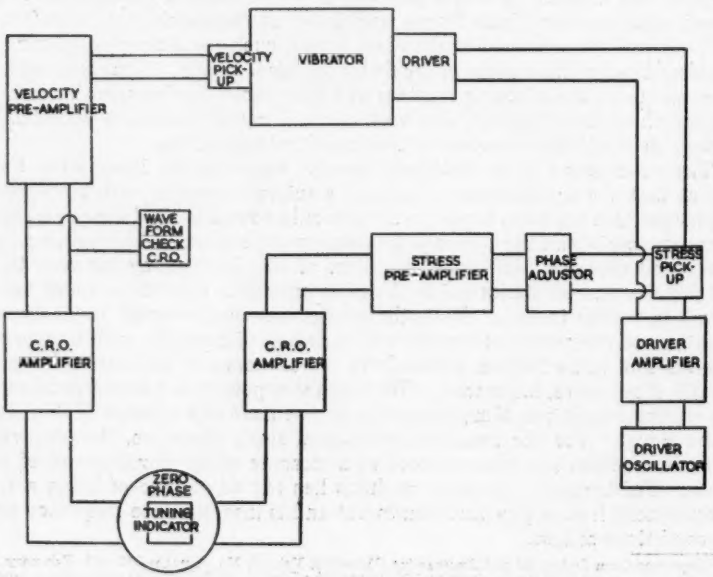

FIG. 1.—Block diagram of compression vibrator.

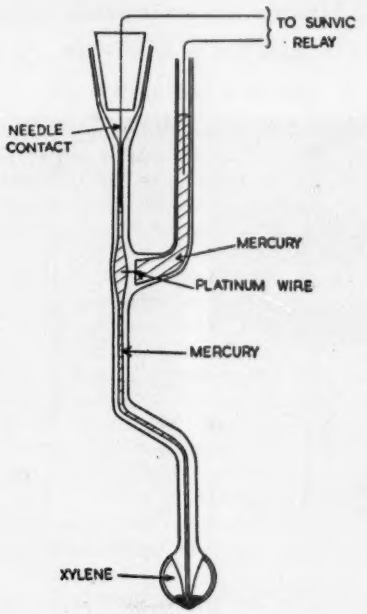

FIG. 2.—Mercury-xylene regulator.

The present work was carried out on the Imperial Chemical Industries' electrical compression vibrator[4] set up in horizontal position and mounted on thick sponge rubber. Figure 1 is a block diagram of the main layout of the experimental equipment. The Muirhead decade oscillator was checked against a known mains frequency and the over-all accuracy of the decade system found to be 0.2 cycle per second.

Temperatures were controlled at $\pm 0.2°$ C by a mercury-xylene regulator (Figure 2) and measured to $\pm 0.5°$ C on two copper-constantan thermocouples, one mounted in the rubber test-piece, the other in the air of the test chamber. A Mullard oscilloscope was used to monitor the wave form of the velocity signal. This procedure gave a check on the alignment of the vibrator. Day-to-day variation in phase shift of the amplifiers was compensated by a phase adjuster network[5] in the stress channel. Tuning to resonance was carried out by a zero-phase method which gives sensitive discrimination.

Figure 3 shows two examples of the closure of the ellipse to the nearest integral cycle. Because amplitude is changing only slowly at the resonance peak, this parameter is effectively constant while the necessary frequency tuning adjustments are made.

The application of the classical theory of forced damped vibrations to rubber has recently been criticized[6] as being not sufficiently general to accommodate the experimental facts. If, however, the changes in conditions in any experiment are kept sufficiently small, the equation can be retained and the previous constants, s (dynamic stiffness) and b (viscous resistance), become functions of the conditions. An equivalence then exists between the two equations for

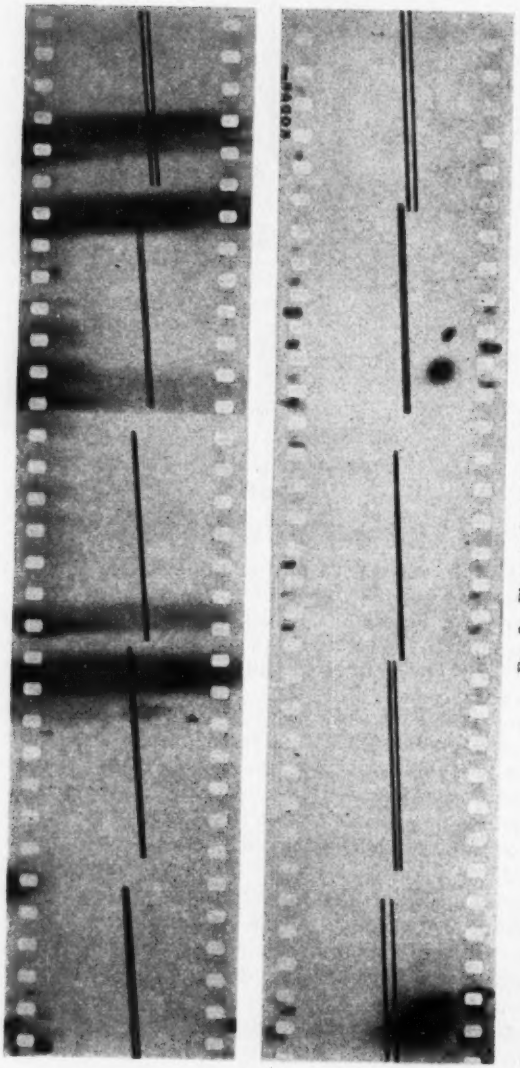

FIG. 3.—Phase tuning to resonance.

alternating mechanical and electrical systems subjected to forced oscillation:

$$m\ddot{x} + b\dot{x} + sx = F \cos pt$$

$$L\ddot{q} + R\dot{q} + q/C = E \cos pt$$

where L, C, and R are the usual electrical symbols and E is the applied e.m.f. In the steady state, therefore, the conditions for velocity resonance (analog of current resonance in the electrical case) are $s = mp^2$ and zero phase difference between applied mechanomotive force and velocity. Also the maximum sensitivity to phase change occurs at resonance and is given by $4\pi m/b$ radians per cycle per second.

In the experimental work every attempt was made to eliminate memory effects[7]. Temperatures were selected so as to get six roughly evenly spaced points between the base-line temperature of about 30° C and a maximum temperature of 70° C. The standard amplitude was 0.0036 cm. The time of test was roughly 45 seconds, and a 10-minute rest was given between each test. The range of frequencies employed was 80 to 170 cycles per second. Bonded samples were used with no static load. Tests were carried out at the different temperatures successively on the same sample to avoid the well known sample variation with rubber mixings involving carbon black. To detect any permanent alteration to the test sample, a standard test of dynamic modulus at the "base-line" temperature was carried out before testing at a new temperature. To avoid marked effects due to chemical changes, no temperatures beyond 70° C were investigated.

For the main investigation compression samples were used, bonded to steel with Vulcabond TX and made in a special mold (mixes R505–511). The rubber specimen in every case was approximately 1.5 inches in diameter and 0.75 inch high. The cure was slightly modified to allow for the thickness of the samples. The unbonded compression samples were made up on a separate occasion (mixes P6410–6413), using a simple three-piece mold.

SELECTION OF BEST CONDITIONS OF TEST

As the methods of testing rubber are refined, it is possible to detect the effect of changing the temperature by 1° C or of changing the vibration amplitude by 10 to 20 per cent.

Many materials are characterized by sharp melting phenomena and relatively well defined physical properties, whereas rubbers[8] tend to change their state by fractions (analogous discontinuities to the Barkhausen effect and similar phenomena[9] in ferroelectrics) over a temperature range that may be extended almost indefinitely. Moreover, the act of measurement is sufficient to cause a small change of state and, hence, a change in physical properties. Relaxation to the previous state, which is measured in any mechanical test, depends not only on the conditions of the test but also on the stress and temperature history of the test-piece. Accordingly it is important to reduce as much as possible both the influence of the test on the property being measured and the memory effects arising from the past history of the test-piece.

The following is a summary of the effects of the various parameters on the dynamic properties measured in this work, and is the basis of the particular test conditions finally adopted.

Static load.—In Table II data are given for the effect of static load on the resonant frequency of a Neoprene Type GN tread stock (P6411, unbonded sample).

TABLE I

COMPOSITION OF MIXES

	P6410 R510	6411 511	6412 508	6413 509	505	506
Perbunan	100	—	—	—	—	—
Neoprene Type GN	—	100	—	—	—	—
Natural rubber	—	—	100	—	100	100
GR-S	—	—	—	100	—	—
Kosmobile-HM (MPC)	50	36	47.5	50	—	—
Kosmos-40 (HMF)	—	—	—	—	—	40
Zinc oxide	5	5	5	5	5	5
Magnesium oxide	—	4	—	—	—	—
Pine tar	3	—	—	3	—	—
Tricresyl phosphate	—	2.5	—	—	—	—
Stearic acid	2	2.5	3	2	1	4
Sulfur	1.5	—	3	2	2.5	3
Mercaptobenzothiazole	—	—	0.85	—	0.5	0.75
Vulcafor-F	1.2	—	—	1.6	—	—
Phenyl-2-naphthylamine	—	2	—	—	—	—
Nonox-S	—	—	—	—	1	1
Basic cure, minutes at 141° C	60	30	45	60	30	45

When bonded samples were substituted, the increase in resonant frequency with static load was much reduced. This was found to apply for all the rubbers investigated, the change in resonant frequency being 1 per cent or less, for a static stress of 2 kg. per sq. cm. Bonded samples under no static load were therefore used throughout the investigation.

Frequency of test.—Table III shows the effect on dynamic stiffness at room temperature and 70° C of altering the frequency of test by a ratio of 1.7 in the range 100 to 300 cycles per second.

Table III shows that there is no significant effect on dynamic stiffness, except possibly in the case of Perbunan. Because this material is known to be

TABLE II

EFFECT OF STATIC LOAD ON RESONANT FREQUENCY

Static stress (kg/ sq. cm.)	Resonant frequency (c.p.s.)
0.7	123.8
1.1	127.5
1.4	128.5
1.8	129.7
2.1	130.7
2.5	130.8
2.8	131.3
3.6	131.7

the most polar of the four rubbers examined and hence to have the highest level of interaction between molecules, the possibility of a frequency effect of the order of 4 per cent at room temperature within the range 160 to 300 cycles per second seems reasonable. Hence for practical purposes in the range of temperatures 25° to 70° C, the frequency effect can be ignored within the actual test range of frequencies employed, *i.e.*, 80 to 170 cycles per second.

Duration of test.—Exercise effect.—Continuous vibration of the test-piece was found progressively to lower the observed dynamic stiffness. Hence a

"jab" technique was adopted, in which the vibration was switched on only for the time necessary to measure the resonant frequency.

Table IV shows the relative constancy of the resonant frequency, when the jab technique was used on a Neoprene sample which had been rested overnight at laboratory temperature.

The jab time was reduced further with the aid of an electronic device to 0.25 second, but without a very great change in the effective dynamic modulus.

It was, therefore, decided to adopt the jab time of about 45 seconds and correspondingly to increase the rest time between readings to 10 minutes. The ratio of the two times must, according to the Boltzmann theory[10], be kept as large as possible to reduce the memory effect to a minimum.

TABLE III

EFFECT OF FREQUENCY ON DYNAMIC STIFFNESS

	Dynamic stiffness × 10^9 dyne per cm.			
	At laboratory temperature		At approximately 70° C	
Material	Weight off (higher frequency)	Weight on	Weight off	Weight on
Natural rubber	2.479	2.478	1.94	1.89
Neoprene Type GN	2.467	2.470	1.96	2.04
GR-S	5.294	5.354	3.06	3.14
Perbunan	4.91	4.68	2.94	2.91

Temperature conditioning.—Even with the jab technique given above, the stiffness was different on the heating and cooling portions of the thermal cycle. To reduce this thermal hysteresis to a minimum, overnight conditioning at the temperature of test was employed. Reproducible results for dynamic stiffness could be obtained in this way at constant temperature, using automatic regulation.

Amplitude of vibration.—In the case of reinforced rubbers, it was noticed early that increased amplitude of vibration caused a decrease in the resonant frequency[11], and this effect has been amply confirmed by other investigators. The interest attaching to the amplitude effect, apart from reproducibility of testing, derives from the fact that, like the temperature effect, it runs counter to the predictions of the simple statistical theory, with no interaction forces. In the present investigation a range of amplitude was therefore studied at each temperature. To minimize memory effects, the value of the resonant frequency was taken on a range of ascending and descending values of amplitude and the true value of the resonant frequency was taken as the arithmetic mean.

TABLE IV

JAB TECHNIQUE FOR CONSTANT RESONANT FREQUENCY

Time (min.)	Resonant frequency using jab of 30 seconds	Temperature of rubber (° C)
0	215.1	19.5
5	215.2	19.5
10	215.2	19.5
15	215.2	19.5
20	215.4	19.5
25	215.6	19.8

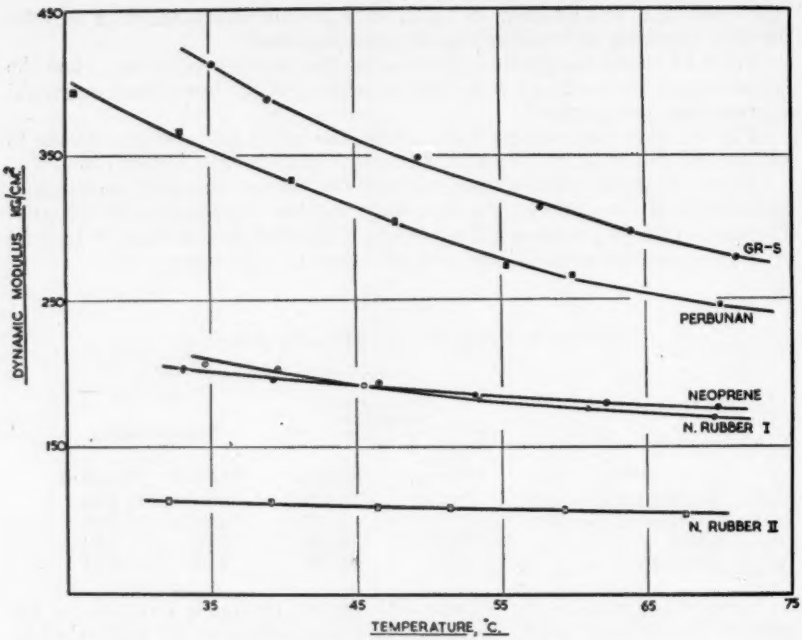

FIG. 4.—Variation of dynamic modulus with temperature. Tread stocks.

DYNAMIC MODULUS

Tread stocks.—Variation of dynamic modulus with temperature at constant amplitude.—Figure 4 shows curves for the four tread stocks, and the natural rubber stock containing 40 parts of a high modulus furnace black (Kosmos-40). On this graph Perbunan and GR-S are well separated, while natural rubber runs very close to Neoprene Type GN. It is clear that within the limited range of temperatures investigated the curves can be considered as exponential in character, and, if a relationship of the type $\gamma = \gamma_0 e^{Q/RT}$ is assumed to hold, it is possible to plot the data in a form from which Q, which has the dimensions of energy, can be calculated. γ is the observed dynamic modulus at absolute temperature T, γ_0 is a constant, and R is the gas constant for 1 gram-molecule. This procedure is shown in Figure 5, where the logarithm of the ratio of modulus at $T°$ C to modulus at 70° C is plotted against the reciprocal of T.

The slopes of the lines are a measure of the apparent activation energy in the temperature range 30° to 70° C. There are, of course, underlying assumptions in applying this type of analysis to data of this kind. It is, for example, assumed that the activation energy is a constant in this temperature range, whereas it is almost certainly a slowly varying function of temperature. The data are not sufficiently accurate to decide this point. The process is assumed to apply to a gram-molecule, a rather indefinite concept when the moving unit may be the carbon particle. From a practical point of view, however, it is still one of the best ways of placing such curves on a quantitative basis.

Considering the slopes of the graphs, while it is not possible to separate GR-S and Perbunan, the other three compounds in general are in the expected order of their reinforcement.

An examination of Table V or VI indicates that the energy barrier is of the order of 0.5 to 2 large calories. It is evident therefore that weak cohesive bonds are responsible for the variation of properties with temperature. Because these forces are of the same order of magnitude as the thermal energy and the applied energy of vibration, measured properties are sensitive to changes in both these parameters.

In any practical application, both the effective dynamic modulus and the rate of change with temperature may be of importance. For example, a GR-S tread is stiffer than a Perbunan tread over the whole temperature range; on the other hand, the level of interaction forces, judged from the apparent activation energies, is similar in the two rubbers. Under these circumstances temperature or exercise might be expected to produce the same relative alteration in properties. If, however, the forces in one rubber were much stronger than in another, the level of modulus might be higher at one temperature and lower at another, *i.e.*, crossovers might occur, and there is some trend in this direction on examining the Noeprene and natural rubber curves, although this difference may be experimental. Furthermore, during the fatigue life of one rubber compared with the other, the relative rates of physical breakdown would be expected to depend on the relative levels of both the interaction forces and the rates of relaxation.

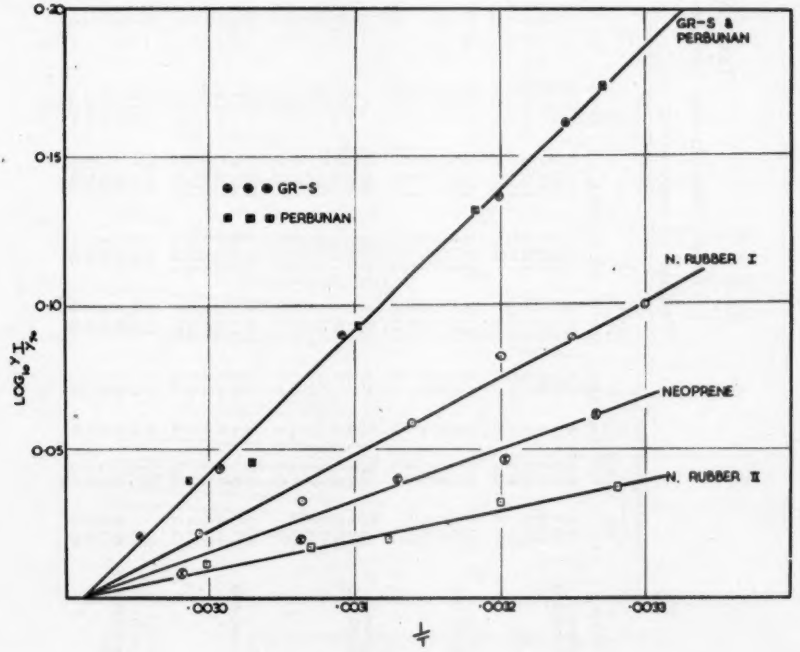

FIG. 5.

TABLE V

DYNAMIC MODULI AND APPARENT ACTIVATION ENERGIES

Rubber	Temperature: Av. (° C)	Temperature: Range (° C)	Frequency (cycles per second): No. of readings	Frequency (cycles per second): Range	Frequency (cycles per second): Av. observed	Frequency (cycles per second): f(B.L.)	Frequency (cycles per second): f(B.L.A.C.)	$\partial f/\partial T$	$a\partial f/\partial a$	Dynamic modulus: $s \times 10^9$ dyne/cm.	Dynamic modulus: $\gamma \times 10^6$ dyne/sq. cm.	Dynamic modulus: γ, kg./sq. cm.	$1/\gamma\ \partial\gamma/\partial T$	$a/\gamma\ \partial\gamma/\partial a$	Apparent activation energy: $\log_{10} \gamma T/\gamma T_0$	Apparent activation energy: $1/T \times 10^{-3}$	Apparent activation energy: Q (kg.-cal.)
Natural tread 508	34.7	0.2	4	0.2	122.1	121.9	121.0	−0.45	− 2.1	−2.43	2.02	206	−0.62	− 3.5	0.0883	0.3250	1.18
	39.5	0.2	6	0.1	120.1	121.1	120.2	−0.45	− 2.1	2.40	1.99	203	−0.60	− 3.5	0.0816	0.3200	
	45.5	0.2	5	0.6	118.1	118.1	117.2	−0.40	− 2.2	2.28	1.89	193	−0.58	− 3.7	0.0592	0.3140	
	53.5	0.2	5	0.2	115.3	114.6	113.8	−0.40	− 2.3	2.15	1.78	182	−0.55	− 4.1	0.0329	0.3053	
	61	0.4	6	0.2	113.0	113.2	112.5	−0.34	− 2.3	2.10	1.74	177	−0.53	− 4.1	0.0221	0.2994	
	69.8	0.5	5	0.3	111.0	110.4	109.8	−0.30	− 2.2	2.00	1.65	169	−0.50	− 4.1	0.0004	0.2917	
Neoprene tread 511	33.1	0.2	6	0.2	121.3	121.0	120.1	−0.39	− 2.7	2.40	2.00	204	−0.41	− 4.5	0.0614	0.3267	0.78
	39.3	0.5	6	0.0	119.7	119.0	118.1	−0.3	− 2.1	2.32	1.93	197	−0.40	− 3.6	0.0465	0.3203	
	46.6	0.2	3	0.0	116.9	118.1	117.2	−0.27	− 2.2	2.28	1.90	194	−0.38	− 3.7	0.0394	0.3129	
	53.4	0.3	4	0.2	114.8	115.4	114.6	−0.26	− 1.7	2.18	1.81	185	−0.37	− 3.1	0.0192	0.3064	
	62.5	1.8	5	0.1	113.9	114.0	113.2	−0.18	− 1.7	2.13	1.76	180	−0.35	− 3.1	0.0073	0.2981	
	70	0.2	6	0.2	113.8	113.0	112.3	−0.16	− 2.4	2.10	1.73	177	−0.33	− 4.2	0.0000	0.2915	
Perbunan tread 510	25.6	0.5	3	0.3	171.1	168.1	166.5	—	—	4.61	3.86	393	−1.24	—	0.2055	0.3361	2.2
	32.8	0.2	6	0.5	157.8	162.4	160.7	−1.3	− 6.1	4.29	3.59	366	−1.18	− 7.7	0.1741	0.3272	
	40.5	0.2	6	0.4	159.4	154.4	153.0	−1.1	−12.4	3.80	3.25	331	−1.12	−16.0	0.1311	0.3183	
	47.9	0.2	6	0.3	144.1	147.5	146.5	−0.8	− 5.6	3.57	2.97	303	−1.06	− 7.7	0.0922	0.3102	
	55.4	0.2	4	0.1	139.7	140	138.9	−0.7	− 3.0	3.21	2.66	272	−1.02	− 4.2	0.0419	0.3030	
	60.0	1.0	5	0.5	135.4	138.8	137.8	−0.6	− 5.9	3.16	2.63	268	−0.98	− 8.5	0.0387	0.2983	
	70.1	0.2	4	0.4	130.6	132.6	131.9	−0.5	− 5.6	2.89	2.40	245	−0.92	− 8.5	1.9996	0.2895	
GR-S tread 509	35.2	0.2	4	0.1	172.4	173.4	172.4	−1.2	− 8.1	4.94	4.04	412	−1.16	− 9.3	0.1622	0.3245	2.2
	39.0	0.2	4	0.4	164.5	168.8	167.5	−1.1	−12.8	4.66	3.81	388	−1.12	−15.0	0.1366	0.3199	
	49.4	0.2	6	0.3	155.6	160.0	158.8	−0.9	− 9	4.19	3.42	348	−1.06	−12.0	0.0802	0.3089	
	57.7	0.2	5	0.5	149.4	152.4	150.6	−0.8	− 5.8	3.77	3.07	313	−1.00	− 7.7	0.0425	0.3008	
	64.0	0.2	5	0.3	144.5	148.6	147.0	−0.6	− 5.7	3.59	2.92	298	−0.96	− 7.7	0.0211	0.2950	
	71.3	0.2	4	0.3	139.4	144.1	142.7	−0.5	− 6.7	3.38	2.75	280	−0.92	− 9.3	1.9947	0.2885	
Natural (less reinforced compound) 506	32	0.2	6	0.1	91.2	90.3	89.6	−0.1	− 1.3	1.33	1.12	114	−0.26	− 2.8	0.0377	0.3281	0.49
	39	0.2	6	0.1	90.2	89.8	89.1	−0.1	− 1.5	1.32	1.11	113	−0.25	− 3.2	0.0324	0.3199	
	46.3	0.2	5	0.1	88.3	88.7	88	−0.1	− 1.6	1.29	1.08	110	−0.24	− 3.6	0.0205	0.3120	
	51.3	0.2	6	0.1	88.3	88.4	87.7	−0.1	− 1.6	1.28	1.07	109	−0.23	− 3.6	0.0171	0.3069	
	59.4	0.2	6	0.1	87.5	87.9	87.2	−0.1	− 1.7	1.26	1.05	107	−0.22	− 3.7	0.0115	0.2990	
	67.5	0.2	6	0.5	86.6	87.0	86.3	−0.1	− 1.6	1.24	1.03	105	−0.21	− 3.4	0.0021	0.2917	

TABLE VI

TEMPERATURE EFFECT (TREAD STOCKS)

Rubber	Dynamic modulus (kg./sq. cm.) γ 35° C	Dynamic modulus (kg./sq. cm.) γ 70° C	% change per ° C $-1/\gamma\partial\gamma/\partial T$ 35° C	% change per ° C $-1/\gamma\partial\gamma/\partial T$ 70° C	Apparent activation energy, Q (kg.-cal.)
GR-S	413	282	1.2	0.9	2.2
Perbunan	352	244	1.2	0.9	2.2
Natural rubber I	208	160	0.6	0.5	1.18
Neoprene	202	168	0.4	0.3	0.78
Natural rubber II	114	105	0.3	0.2	0.49

Table V gives two estimates of the temperature coefficient. The column labeled $\partial f/\partial T$ gives the cycles per second change in the resonant frequency per ° C. The values have been obtained by graphical differentiation of Figure 4 and are approximate only. The largest changes per ° C are with GR-S and Perbunan and are about 1 cycle per second per ° C, so a temperature change of 1° C is easily noticed. With the less reinforced natural rubber compound, 1° C does not produce a practically observable difference. The second estimate is probably more accurate and has been calculated from the value of the apparent activation energy. The units are percentage change of modulus per ° C and are in the column headed $1/\gamma\partial\gamma/\partial T$.

Variation of dynamic modulus with amplitude at constant temperature.—Figure 6 shows the changes of resonant frequency (proportional to square root

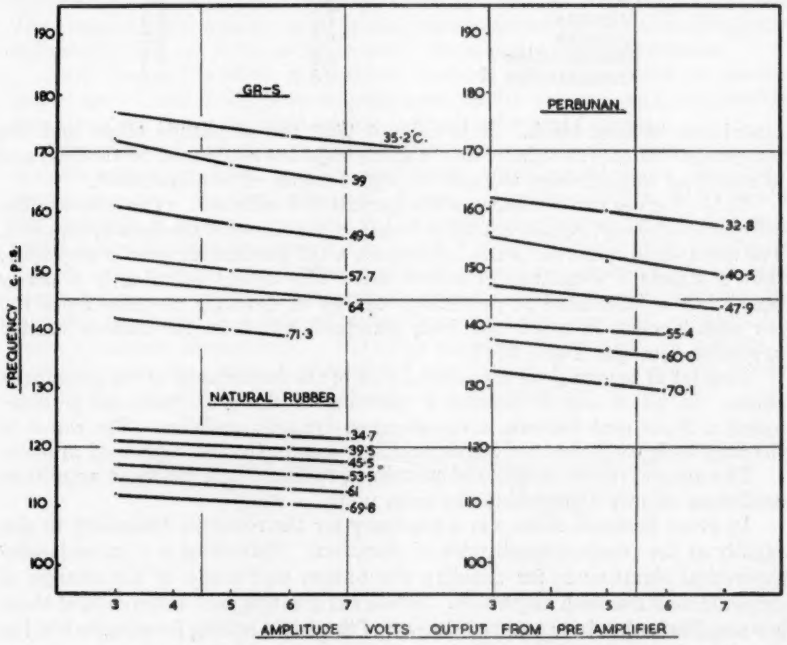

FIG. 6.—Variation of resonant frequency with amplitude and temperature.

of dynamic modulus) with amplitude at constant temperature for three of the five rubbers. Neoprene and the less reinforced natural rubber would have to be plotted on a larger scale, as the lines are too close.

Only a part of the experimental data has been plotted, where the frequency tends to vary linearly with amplitude. At lower amplitudes the frequency was always found to rise sharply, as was also observed in the experimental work of Oberto and Palandri[12], and it was thought that frictional effects might be responsible. When the current in the driver coil was plotted against amplitude of vibration, definite evidence of friction in the test apparatus at the lowest amplitudes was present.

Examining the amplitude effect as a whole, the following facts emerge:

In every case a set of nearly parallel curves (drawn as straight lines over the limited range of amplitude on the graphs) is obtained.

The variation of the amplitude effect with temperature is secondary. In one or two cases the slopes alter with temperature in a random manner.

The average slope of the set of curves is greatest with GR-S and Perbunan. The next pair are natural rubber and Neoprene. The flattest is the compound

TABLE VII

AMPLITUDE EFFECT (TREAD STOCKS)

Rubber	% Modulus change for doubling amplitude, $-a/\gamma\partial\gamma/\partial a$	
	35° C	70° C
GR-S	9.3	9.3
Perbunan	7.7	8.5
Neoprene	4.5	4.2
Natural rubber I	3.5	4.1
Natural rubber II	2.8	3.4

containing furnace black. It is evident that the amplitude effect and the temperature effect run side by side in going from one compound to another, and in a general way increase with the expected degree of reinforcement.

Table V gives two estimates of the amplitude coefficient. The first is in the column headed $a\partial f/\partial a$ and is a value based on the slopes of the lines in Figure 6. The units are in cycles per second change for a 100 per cent increase in amplitude from a standard amplitude of 0.0036 cm. The second estimate is similarly based, but is calculated as percentage change in dynamic modulus for a 100 per cent increase in amplitude from standard, and is in the column headed $a/\pi\partial\pi/\partial a$ (see also Table VII).

This set of figures gives a practical idea of the importance of the amplitude effect. In GR-S and Perbunan, a doubling of the amplitude can produce nearly a 10 per cent decrease in the observed dynamic modulus. The values of the amplitude coefficient are correspondingly less for the less reinforced rubbers.

The natural rubber compound containing furnace black shows an amplitude coefficient of only 3 percent in the same units.

In every instance there was a tendency for the resonant frequency to rise rapidly at the smallest amplitudes of vibration. This effect is of considerable theoretical significance for deciding the nature and origin of the change of dynamic modulus with amplitude. While the greatest part of the data at these low amplitudes has been omitted because of the doubt arising from static friction already mentioned, Figure 7 has been included because the observed variation

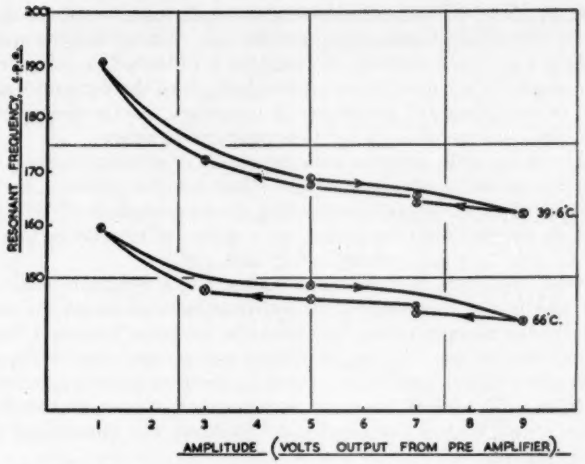

FIG. 7.—Variation of resonant frequency with amplitude of vibration. GR-S tread.

of amplitude with driving current showed that static friction was nearly absent. It will be seen that the same turn in the resonant frequency is present at low amplitudes. These experimental results on GR-S at two temperatures of 39.6° and 66° C show an amplitude freezing phenomenon analogous to the temperature stiffening, and suggest a common origin of the two variations. The characteristic memory effect is also well shown by the points on the graph, indicated by arrows in the order in which the measurements were taken.

Gum stock.—Variation of dynamic modulus with temperature at constant amplitude.—Table VIII shows experimental results obtained on a natural rubber gum stock using the same testing method as for tread stocks.

The observed variation in frequency with temperature is seen to be of a random nature and must be attributed to the experimental error. Because it was obvious that the effect was small, it was decided to obtain a better idea of the variation, if present, by omitting the overnight conditioning and doing the whole temperature variation in a single day. This would minimize the experimental error without introducing large memory errors, because these are least in gum stocks. The figures obtained are shown in Figure 8, where the dynamic modulus is plotted in arbitrary units (square of the observed resonant frequency) against temperature. With this experimental method an increase in modulus with temperature is observed as expected from the simple kinetic theory, the points falling approximately on a straight line.

TABLE VIII

TEMPERATURE EFFECT (NATURAL RUBBER GUM STOCK)

Temperature (° C)	Resonant frequency (c.p.s.)
20.4	78.7
33.1	77.6
41.2	77.4
47.3	78.4
57.6	77.7
65	77.6
78	78.5

The amplitude of vibration in these gum stock tests was more than double that used for the tread stocks, being 0.0095 cm. Under these conditions, approximately a 4 per cent increase in modulus is obtained in going from 40° to 70° C. To establish the exact form and magnitude of the variation, still further refinement in experimental technique is necessary, as the frequency is only altered 2 cycles per second for a 30° C temperature change.

Variation of dynamic modulus with amplitude at constant temperature.—The evidence on the direction of the amplitude effect was inconclusive, and varied on different days. In approximately doubling the amplitude the following changes were noted in the resonant frequency at a series of increasing temperatures: −1.1, −2.1, +0.07, +0.3, −0.08, −0.2, and −0.2.

In the measurements of Oberto and Palandri[12], a dynamic tension modulus was found which was independent of dynamic tension strain for gum stocks, while in the shear measurements the dynamic modulus increased linearly with the dynamic shear strain. If the amplitude and temperature effects are analogous in different rubbers, one would expect an increase in dynamic modulus with dynamic strain. The effect, however, is very small, if one assumes that as with tread stocks a doubling of the amplitude produces the same effect as a 10° C rise in temperature.

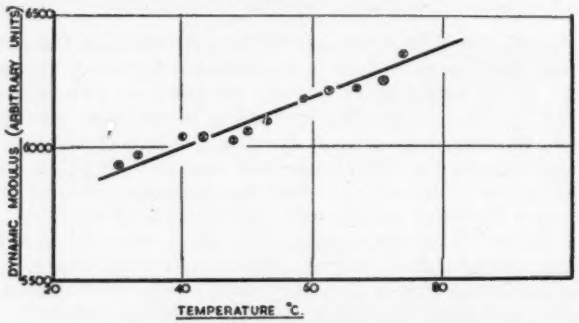

FIG. 8.—Variation of dynamic modulus with temperature. Natural rubber gum stock.

ELECTRICAL RESISTIVITY UNDER VIBRATION

To get further evidence on the phenomenon of the alteration of modulus with amplitude of vibration, exercise, and temperature, measurements were made of the electrical resistivity of a bonded rubber specimen under various conditions. In the case of natural rubber, the specific resistivity was of a suitable size for simple measurements, being about 2.5×10^8 ohms. A voltage of 75 gave a deflection of 300 to 400 divisions with a D'Arsonval galvanometer, having a sensitivity of 230 divisions per microampere.

A number of measurements done on different days on the same specimen established that there was an increase in conductivity with temperature when no vibration was present. At an early stage, it was found that the presence of mechanical vibration increased the resistivity by as much as 10 per cent at the highest amplitudes studied, approximately 0.013 cm. This effect parallels under vibration conditions the effect noted for some time of the increase of resistivity under simple flexure investigated by Bulgin[13]. Bulgin noted also the phenomenon of two temperature coefficients, depending on whether the

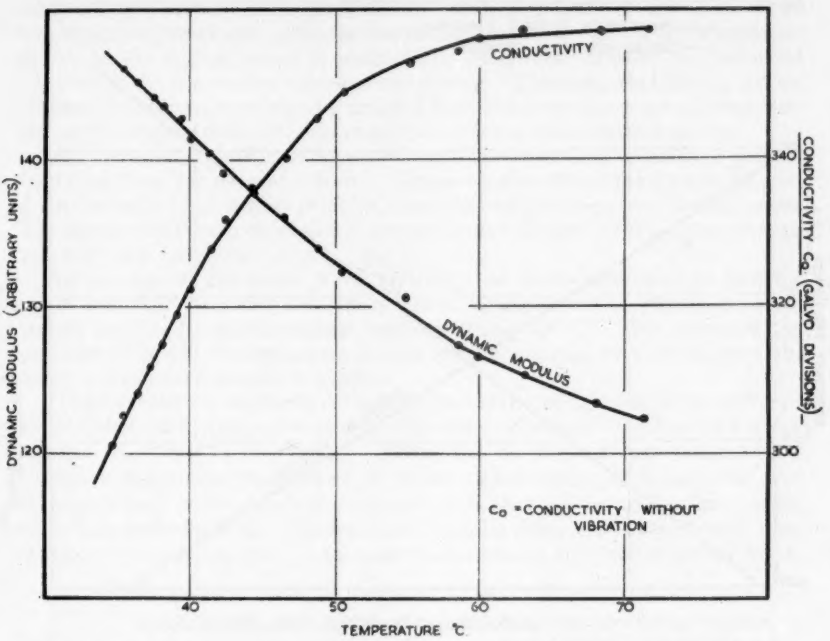

FIG. 9.—Effect of temperature on dynamic modulus and electrical conductivity. Natural rubber tread.

sample had previously been flexed or not. This probably explains the difficulty of getting reproducible results (on different days) for the temperature variation. When measurements were done on a cooling curve taking 3 hours (sufficiently slow to allow a fair approach to equilibrium), the variations with temperature of modulus and conductivity (with no vibration applied) shown in Figure 9 were obtained. In the modulus measurements the vibration amplitude was standard.

As the dynamic modulus increases with falling temperature, the conductivity falls. When, however, the change in conductivity (Co-C), due to applying vibration to the rubber test-piece is measured, it is found to increase with increased energy input. In consequence if $\sqrt{Co-C}$ is plotted against amplitude, the resulting graph is approximately linear (Figure 10). In comparing Figures 9 and 10, it will be noted that increasing temperature causes increased conductivity, while increasing amplitude of vibration causes the conductivity to drop progressively (shown in Figure 10 by $\sqrt{Co-C}$ becoming greater). On the other hand, however, both increasing temperature and increasing amplitude of vibration produce a decrease in modulus.

The apparent contradiction of the conductivity results can readily be understood in terms of a dual effect of temperature. It has been pointed out[13] that the conductivity of the carbon network itself increases with temperature. On the other hand, the increased kinetic energy of Brownian motion can cause a decrease in the total number of cohesive bonds in the structure, resulting in decrease of modulus and increased resistivity (decatenation). It would appear

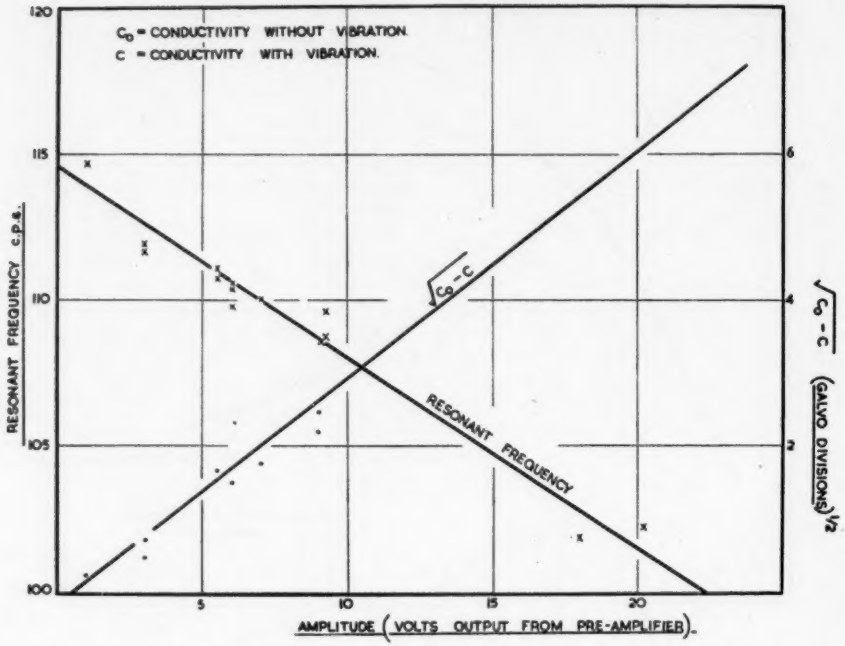

FIG. 10.—Effects of variation of amplitude on resonant frequency and conductivity. Natural rubber tread, 72° C.

that decatenation is the main result of mechanical vibration, while a rise in temperature can cause both effects, with the increase of conductivity of the carbon structure predominating.

An interesting conclusion can be drawn definitely from these results on conductivity with natural rubber, which is difficult to deduce from the mechanical measurements alone. The effect of amplitude of vibration on the dynamic modulus is not due to the rise in general temperature of the specimen; if this were so, the conductivity of the carbon structure would be expected to increase, whereas it is found actually to decrease and in addition the amount of the decrease is more marked, the greater the amplitude of vibration. This is convincing proof that decatenation does take place when vibration is applied and that it is in part responsible for the drop in modulus and conductivity in the natural rubber tread stock. When Perbunan was investigated, the conductivity was found to be much less (about 15 per cent) and no detectable change was found when the largest vibration was applied. It may be that some effect is there, but it is proportionately less than in the case of natural rubber. This suggests that the drop in modulus with Perbunan on increasing the temperature or amplitude of vibration may be due mainly to the rupture of rubber-rubber cohesive bonds, or more likely carbon-rubber, neither of which would appreciably affect the electrical conductivity.

In the case of GR-S, the effects were parallel to those observed with natural rubber, though the conductivity level was much reduced, and was of the same order as Perbunan. The relative drop on applying vibration was also some-

what smaller, even after allowing for the lower amplitude of vibration, 0.008 cm. instead of 0.014 cm. One further difference noted was the more rapid recovery to the original value of conductivity when the vibration was switched off, though the recovery of modulus was slower. This suggests that the carbon cohesive bonds heal more rapidly in GR-S than those which are mainly responsible for the drop in modulus, presumably the carbon-rubber attachments.

An examination of Figure 11 shows that this decrease in modulus is greater for GR-S than for natural rubber. Figure 11 also shows the change in conductivity of natural rubber samples, measured while fatigue was taking place. The corresponding curve for GR-S has not been included, as the actual change was only two divisions.

In the case of Neoprene, a conductivity was observed similar to that for GR-S and Perbunan, but here there was no change even on vibrating at the largest amplitudes at laboratory temperature or 70° C. This indicates the presence of less carbon structure in this tread compound and the relative absence of weak carbon-carbon bonds.

These results on conductivity indicate a method of analysis of the different types of cohesive bond responsible for the final reinforced structure in a given natural or synthetic compound. Alterations in modulus are produced by change in the number of bonds of all types, rubber-rubber, carbon-rubber, and carbon-carbon, while electrical conductivity is affected mainly by the number of carbon-carbon bonds. Furthermore, judging from experiments with gum stocks, it is probable that at elevated temperatures the rubber-rubber bonds

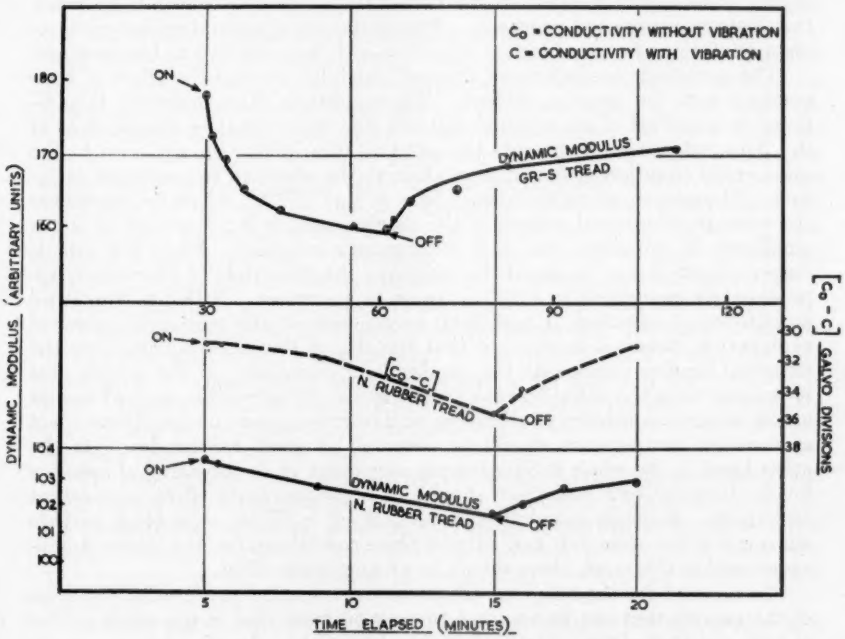

FIG. 11.—Effect of exercise on dynamic modulus and conductivity. Natural rubber and GR-S treads, 70° C.

are on the whole less important, so measurements at temperature extremes should separate the individual contributions from the rubber-rubber and carbon-rubber bonds.

In all the electrical data given so far, the alteration in the mean conductivity has been measured. It was interesting to see whether any idea of the time factor involved in these changes could be arrived at by trying to detect an alternating component. This was done by completing the circuit through a 200,000-ohm resistance in the same valve voltmeter as was the pickup signal. Under these conditions a ripple of the vibrating frequency was observed on a cathode ray tube of amplitude equivalent to about 10 per cent of the mean alteration indirect current conductivity.

This implies that the alteration in conductivity can follow to a limited extent the applied vibration at 120 cycles per second.

CONCLUSIONS

The dynamic modulus of tread stocks changes with temperature in a way which resembles the variation of viscosity of liquids with temperature. This indicates the existence of potential barriers of the order 0.5 to 2 kg.-cal. which can be attributed to the presence of weak cohesive bonds of a van der Waals nature. Qualitatively the height of the barrier increases with the expected degree of reinforcement in the range of rubbers investigated, being greatest with GR-S and Perbunan and least with natural rubber and Neoprene. In making this estimate some account must be taken of the low tensile strengths of gum stocks made from GR-S and Perbunan in comparison with those made from natural rubber and neoprene. The compound of natural rubber containing a reinforcing furnace black is, of course, still less sensitive to temperature.

The amplitude coefficients of dynamic modulus parallel the effect of temperature over the range of rubbers. The amplitude effect, however, is additional to the effect of temperature and to a first approximation independent of it. This independence suggests the addition of a further energy term to the exponential equation discussed in relation to the observed temperature variation. The new equation would then be $\gamma = \gamma_0 e^{Q/(kT+ba^2)}$, where ba^2 represents the average vibrational energy of the moving unit, b is a constant, a is the amplitude of vibration, and k is Boltzmann's constant. From the experimental results it may be noted that doubling the amplitude of vibration is approximately equivalent to a 10° C rise in temperature. If this is true at all amplitudes of vibration, it is difficult to conceive of any reasonable physical explanation, unless it is assumed that the size of the units moving over the potential barriers varies with the amplitude of vibration. If the moving unit is assumed to be the individual gas black particle, ba^2 is found to be $\ll kT$ except at the largest amplitudes of vibration, and in consequence no amplitude effect at constant temperature should be observed at small amplitudes. On the other hand, if the whole rubber sample cooperates in the breaking of cohesive bonds, then $ba^2 \gg kT$ and there should be no temperature effect at constant amplitude. A simple calculation shows that $ba^2 = kT$ for a gas black particle when a is of the order 0.01 cm. Under these conditions, *i.e.*, the largest amplitudes used in this work, there should be an amplitude effect.

To account for the observed effects at much smaller amplitudes, the mass of the moving unit can be assumed to vary between that of the whole rubber sample and that of the individual gas black particle. As the vibration amplitude is increased, one must visualize the structure as being progressively broken

down and the effective mass of the moving unit being altered according to an equation of the type $m = m_0 f(a)$, where m is the effective mass of the moving unit, m_0 is a constant, and $f(a)$ is a function depending on the amplitude of vibration, a thixotropic function, whose form could be determined by a more exact examination of the variation of modulus with amplitude of vibration. During a determination of dynamic modulus, from the time of switching on, there is a tendency for an equilibrium to be established between this breakdown of structure and the effort to relax to the previous condition. A dynamical equilibrium is thus achieved which is responsible for the particular value of the observed modulus.

This analysis of the amplitude effect accounts also for the observed efficiency (from an energetic viewpoint) of small amplitude vibrations (low energy) in reducing the dynamic modulus of the rubber under test. Production of an equivalent effect by a rise of temperature of the test piece needs a far greater amount of energy.

This effect of small amplitudes of vibration in reducing the dynamic stiffness is thus compared to thixotropy in a colloidal system. Vibration can produce a breakdown in the structure due to the effect of orientation in the mechanical field. In contrast, increased temperature is random in direction and any thixotropic effect is in consequence reduced. The effect of temperature must, therefore, mainly rely on actual breakage of cohesive bonds, while vibrational thixotropy can produce aligning effects among structural units (molecular or colloidal), which are evident in an effect on the viscosity (and hence on effective dynamic modulus) at relatively small amplitudes of vibration.

There is no complete mathematical theory of thixotropy, but recovery after removal of stress is one of its chief characteristics. This is the fundamental basis of the history or memory effects noted in these investigations. The frequency of the vibration must be more rapid than the relaxation time of the structure resulting from the vibration if any progressive effect is to be observed. This structure is again clearly shown in the exercise effect and the recovery on resting. Furthermore, recovery, as in the corresponding creep phenomena under static loads, is initially rapid and thereafter much slower. There does seem evidence for the view that the relaxation spectrum of a material is not characterized by its initial state alone, but is a function of the initial and subsequent states during test. One would, therefore, conclude that the quickest recovery is from the shortest stress history, in agreement with the theory of Boltzmann and the experimental evidence of the jab and rest techniques.

Thixotropy is favored by anisodimensional particles. The chain structures which occur with carbon black are ideal in this respect. Thixotropy has been postulated to explain many similar phenomena, for example, the creaming of latex. Generally it is considered that a second potential minimum exists in the field of force between thixotropic particles, so that a reversible change of phase can take place between the two[14].

The comparison of the effects of amplitude of vibration on mechanical and electrical properties suggests that, though the amplitude effect is shown with all the tread rubbers examined as far as mechanical properties are concerned, it is absent or much reduced in Neoprene and Perbunan for electrical properties. This suggests the relative absence of carbon chains sufficiently long to be adlineated by the vibration.

Possibly the thixotropic structures in the case of these two rubbers are connected through rubber-carbon connections, and not carbon-carbon. On the other hand, it may be argued that the absence of conductivity change on vibra-

tion is caused by a balance of increased conductivity due to adlineation and reduced conductivity due to breakage of chains of carbon particles.

Although there is a general parallelism between the effects of amplitude and temperature on dynamic modulus which suggests a common origin in the existence of potential barriers in these materials, two points of difference must be emphasized: the greater efficiency of small vibrations in promoting passage over these potential barriers, and the opposite signs of the temperature and vibration coefficients of conductivity. Increased temperature produces increased conductivity, while increased amplitude of vibration, in those cases where a definite effect was observed, reduced the conductivity.

This suggests that, at least as far as the black structure is concerned, the effects of temperature and vibration differ qualitatively.

If the existence of two states of the carbon black structure are postulated, one of which has a higher and the other lower conductivity and modulus, vibration is visualized as promoting a thixotropic change from the one to the other. On the other hand, temperature due to its random nature is presumed to have a mixed effect. The increased kinetic energy of Brownian motion causes on balance a relaxation of the black structure (catenation)—a view presented by Bulgin[13]—and at the same time a breakdown of the cohesive bonds between carbon and rubber, which do not affect the conductivity, but contribute a considerable amount to dynamic modulus. There is, of course, the effect of temperature on the conductivity of carbon itself; while this is in the right direction, the usual figures given for the temperature coefficient of graphitic carbon are not sufficiently high to account for the observed effects.

The experimental results given here, particularly the actual size of the activation energies, 0.5 to 2 kg.-cal., confirm the general views outlined by Blanchard and Parkinson [15], that the changes in properties of tread vulcanizates are due to changes in what they call the fortuitous structure. The main implication in this term is that the structure is of a weak and changing nature.

Beyond this general agreement, however, certain important differences must be emphasized with respect to the particular conclusions to be drawn from these experimental data and those of the investigators referred to above. Blanchard and Parkinson conclude that prestressing "breaks relatively weak fortuitous chain structures, formed by reversible van der Waals forces between particles which contribute little to the stiffness except perhaps at small stresses," and state that "prestressing has little if any influence on tensile strength but lowers abrasion resistance. Tests on the Dunlop constant energy abrasion machine on the vulcanizate used in the present investigation indicate a decrease of about 20 per cent after 250 per cent prestretch."

The lowering of resistance to abrasion suggests that the fortuitous structure may contribute to factors of great technological importance. This is amply confirmed by the results on dynamic modulus and conductivity of a natural rubber tread stock reported here; the modulus increases rapidly at small amplitudes, indicating the presence of an effectively hard structure under conditions which must simulate tire service more nearly than most of the traditional tests. Furthermore, tread stocks are employed under conditions that emphasize the maximum dynamic modulus. As has been shown in these investigations, higher values of dynamic modulus are obtained by having a large ratio of resting time to the time of successive tests.

This is just the condition that prevails in a tire. No matter what the speed of the tire, the time of impact is some ten times less than the rest peroid between successive impacts; this gives plenty of time for considerable recovery from the

breakdown of cohesive bonds due to impact of a portion of the tire tread pattern with the road before the same part comes around again.

The lack of correlation between road service and most abrasion tests in the laboratory, which still prevails[16], may also arise from the same source. If the diameter of the test wheel in the laboratory machine is much smaller than an actual tire, so as to speed up testing, it is hardly possible to match road speed and test time between successive impacts at one and the same time.

The different reinforcing effects of the same carbon black in the four rubbers as assessed by the various experiments described may appear mutually contradictory or in conflict with the general picture as gained from a study of the more usual tests.

Table IX summarizes by a method of (+) and (−) the way in which the

TABLE IX

TYPES OF COHESIVE NETWORK IN TREADSTOCKS

	Type of cohesive network					
	R-R		C-C		C-R	
	Magnitude of strain					
	Low	High	Low	High	Low	High
Natural rubber	−	+	+	−	−	−
Neoprene Type GN	+	+	−	−	−	−
GR-S	+	−	+	−	+	+
Perbunan	+	−	−	−	+	+

essential facts can be accounted for by the hypothesis that the four rubbers divide into groups with varying emphasis on the three main types of cohesive network, R-R (rubber-rubber) C-C (carbon particle chains of great length), and C-R (carbon-rubber structure, including short carbon chains). This process of division may be expected to vary with the magnitude of the strain. In Table IX the two extremes are taken—high, as may occur in an ordinary tensile strength test, and low, as may be expected in vibration experiments.

The following facts are consistent with this table:

R-R network.—The dynamic modulus of gum stocks of the four rubbers corresponds to the grouping in column 1, *i.e.*, the dynamic modulus for natural rubber is lower (−) than for the three synthetics (+) which have similar values.

The tensile strength of gum stocks of the four rubbers is given by the grouping in column 2. The difference from column 1 is to be attributed to crystallization effects in natural rubber and Neoprene Type GN.

C-C network.—The effect of vibration on electrical conductivity gives the grouping in column 3, where at low strains natural rubber and GR-S are grouped together as giving an effect (+) and Neoprene Type GN and Perbunan show no effect (−); (−) in column 4 indicates the relative weakness of this network in all four rubbers under high strains.

C-R network.—Columns 5 and 6 support the theory that the main C-R structure persists at all elongations, with approximately the same emphasis in the different rubbers.

By adding (+) and (−) horizontally at low strains, the order of the dynamic modulus in tread stocks is given for the four rubbers. The same addition performed at high strain predicts that the level of the tensile strength for all four rubbers is of the same order.

The effect of moderate variations in temperature and amplitude of vibration is to break up the weaker bonds which are present in both the C-C and C-R networks, without altering the observed order of dynamic modulus of the four rubbers.

Unusual temperatures, *e.g.*, subnormal, might produce marked changes in the order by emphasizing the R-R structure.

SUMMARY

The measurements were undertaken to obtain a better understanding of the mechanism of the reinforcement of rubber by carbon black.

Results are given for the dynamic compression modulus and its temperature and amplitude coefficients, in the temperature range 30° to 70° C and at amplitudes of vibration around 0.0036 cm., for natural rubber, Neoprene Type GN, GR-S, and Perbunan. Data are also given on the effect of vibration and temperature on electrical conductivity.

The results are discussed in relation to the general level of reinforcement. Evidence is given for the rupture of more than one type of cohesive bond in repeated cycles of vibration. A tentative system of analysis is proposed. The different effects of temperature and continuous vibration on dynamic modulus are attributed to a thixotropic breakdown in the case of vibration. The significance of such a "structure" dynamically hard at small amplitudes of vibration, is related to abrasion of tires in service.

NOMENCLATURE

Range = difference between highest and lowest readings
$f(B.L.)$ = frequency corrected for base-line variation
$f(B.L.A.C.)$ = frequency corrected for base line, amplitude, and oscillator calibrations
s = dynamic stiffness
γ = dynamic modulus
Q = apparent activation energy, kg.-cal.
T = absolute temperature
γT_0 = dynamic modulus at 70° C
γT = dynamic modulus at T° C
$a/\gamma \ \partial\gamma/\partial a$ = % change in modulus for 100% increase in amplitude from standard
a = amplitude
$a \ \partial f/\partial a$ = change in frequency, cycles per second for 100% increase from standard amplitudes
$\partial f/\partial T$ = frequency change, cycles per second per ° C

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RELAXATION PROCESSES IN THE DEFORMATION OF UNLOADED RUBBERS AND THE INFLUENCE OF THE DEGREE OF VULCANIZATION *

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As was shown in preceding articles[1], a study of the relaxation phenomena which are associated with high elastic deformation is of interest as a means of demonstrating several peculiarities of the structure which determine the physical state of the polymer under the experimental conditions; in addition, such a study has an immediate practical value. In particular, in this earlier work the relation between the relaxation properties and the nature of intermolecular reactions of polymers was shown.

The theories developed in the earlier work led to a quantitative expression of the kinetic laws of high elastic deformation and to certain considerations regarding the relation between the factors which determine the relaxation properties and energy and also the concentration of elementary bonds concerned in the van der Waals reaction between the chains of the polymer. It should be noted, however, that the experimental results hitherto obtained refer principally to linear polymers (smoked sheet rubber, brominated rubber), and to the simplest relaxation relationships between stress and time when the given deformation remains constant.

The present work is concerned with an investigation of the relaxation processes in 3-dimensional polymers. For this purpose a series of unloaded rubbers containing 2 per cent of sulfur and vulcanized for different periods was studied. The aim of this work was also to ascertain the applicability of the previously proposed kinetic equation of high elastic deformation[2] to the representation of a number of complicated deformation systems and particularly of systems where stretching is at a constant rate.

Unloaded vulcanizates of smoked-sheet rubber and various synthetic elastomers were used in the investigation. In Table 1 the types of rubbers studied are given, and symbols used for the various vulcanizates are listed.

Table 1

Types of Rubber and Symbols Representing Them

Time of vulcanization at 143° C (min.) (Mercaptobenzothiazole as accelerator)	Types of rubber				
	HK	CK-1	CK-2	CK-3	CK-4
5	03/5	05/5	06/5	09/5	10/5
10	03/10	05/10	06/10	09/10	10/10
20	03/20	05/20	06/20	09/20	10/20
40	03/40	05/40	06/40	09/40	10/40
60	03/60	05/60	06/60	09/60	10/60

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Colloid Journal* (USSR), Vol. 13, No. 1, pages 11–19 (1951).

EXPERIMENTAL PART

Stress relaxation at a given deformation.—Stress relaxation at different deformations (not exceeding 600 per cent) and temperatures (between 20° and 70° C) was first studied.

Applying the general kinetic equation of high elastic deformation[3]:

$$\frac{d(\sigma - E_{\sim}\epsilon)}{dt} = (E'_0 - E_{\sim})\frac{d\epsilon}{dt} - \frac{\sigma - E_{\sim}\epsilon}{\tau} \tag{1}$$

where

$$\tau = \tau^* exp[-\beta(\sigma - E_{\sim}\epsilon)^2] \tag{2}$$

(using in this particular case ϵ = constant), the form:

$$-\frac{d\sigma}{dt} = \frac{\sigma - E_{\sim}\epsilon}{\tau} \tag{3}$$

can be verified by the method already described[4].

Equations (1) and (2) are valid within a limited range of temperature, rate of deformation, and experimental time, when the initial modulus E'_0 remains at a low value. This indicates a high elastic mechanism of deformation when there is no rupture of the chemical bonds, which would cause a permanent structural change and unlimited relaxation of stress ($\sigma \to 0$).

In the equations given, σ and $\sigma_{\sim} = E_{\sim}\epsilon$ are the instantaneous and equilibrium stresses; ϵ is the deformation, t is the time; E'_0 is the initial modulus, $E_{\sim}$ the equilibrium modulus of high elasticity, and τ is the relaxation time, which, according to Equation (2), is itself a function of the unbalanced stress.

The values of τ^* and β in Equation (2) are found through Equations (4) and (5):

$$\tau^* = \tau_0 exp\frac{u_0}{kT} \tag{4}$$

$$\beta = \frac{V}{2E_1kT} \tag{5}$$

where τ_0 is a constant which is independent of experimental conditions; u_0 is the energy of activation of the elementary structural change which constitutes relaxation, V is the (volume of the) kinetic element of relaxation, k is the Bolzmann constant; T is the absolute temperature, and $E_1 = E'_0 - E_{\sim}$ is the modulus of the unbalanced part of the instantaneous high elasticity.

The linear relation between the logarithm of the time of relaxation and the square of the unbalanced stress, according to Equation (2), was considered a criterion of the applicability of Equations (3) and (2) to the representation of the stress relaxation. Accordingly the time of relaxation was measured from the stress-time curves according to the equation:

$$\tau = -(\sigma - \sigma_{\sim})\left(\frac{\Delta\sigma}{\Delta t}\right)^{-1}$$

according to Equation (3) (method of finite differences).

The method of determining the equilibrium stress $\sigma_{\sim}$ is not given here, since it was previously described in detail[3].

As would be expected, for all the rubbers studied the quantity $(\sigma - \sigma_{\sim})^2$ $\log\tau$ closely approximates a linear value. This establishes the applicability of the foregoing equations to the quantitative representation of stress relaxation in 3-dimensional polymers and in unloaded rubbers in particular.

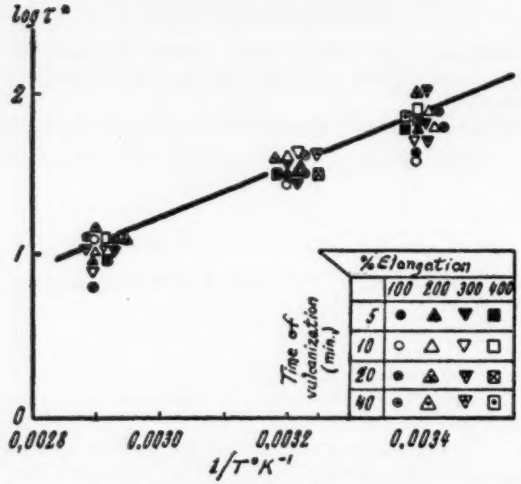

FIG. 1.—Total time of relaxation, τ^*, after different elongations as a function of the temperature (05 rubber vulcanized to different states).

Consequently, the experimental values of τ^* and β make possible a thorough investigation of the relaxation properties of a material and of the influence of the experimental conditions. Figure 1 gives the values of τ^* and Figure 2 gives the values of β obtained from experiments at different deformations and temperatures for vulcanizates of SKB-1. Figures 3 and 4 show similar relation-

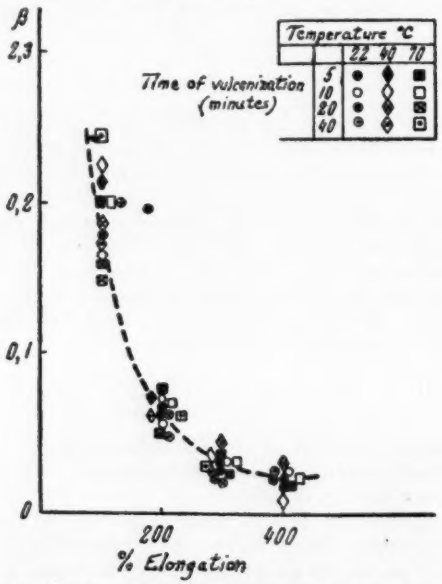

FIG. 2.—Relation of β to deformation for different temperatures (05 rubber vulcanized to different states).

ships for all the rubbers studied. Compensations were made for the elongation, temperature, and time of vulcanization as in the curves of Figures 1 and 2.

The data given confirm beyond doubt the observation made earlier[3] that the total time of relaxation τ^* does not depend on the deformation, but does

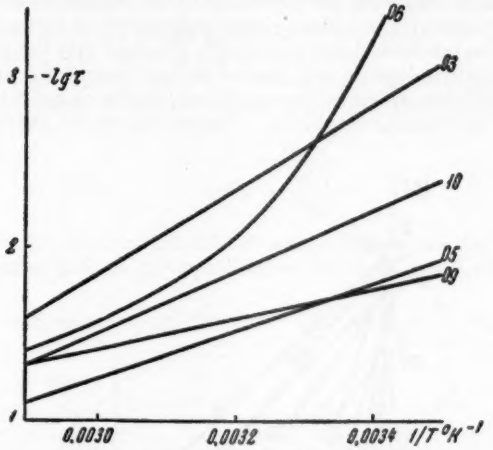

FIG. 3.—Relaxation time limit τ^* as a function of temperature for different rubbers (06, 03, 10, 05, 09).

decrease regularly with the temperature in accord with Equation (4)[5]. As for the constant β, within the range of experimental accuracy it does not depend on the temperature, but decreases sharply during deformation. This observed

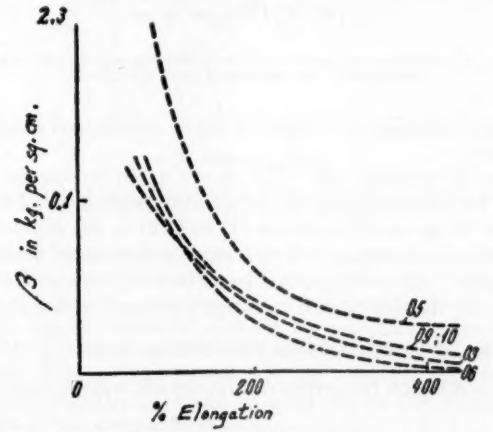

FIG. 4.—Relation of factor β to deformation for different rubbers (06, 03, etc.).

change of β with deformation also agrees with the observations made earlier[3] concerning unvulcanized smoked-sheet rubber and brominated rubber.

The fact that the values of τ^* and β for any given deformation and any given temperature remain constant during vulcanization is quite new.

In Figures 1 and 2 the points corresponding to the different times of vulcanization are given. It is evident that there is no regular change during the vulcanization process for either relaxation property. The results obtained in this part of the experimentation for the other mixtures are exactly the same.

The conclusion regarding the constancy of the relaxation properties of soft rubbers during vulcanization seems rather unexpected at first glance, and complete data will be furnished below as proof. The fact that the relaxation properties of unloaded rubbers do not depend on the time of vulcanization means that the τ^* and β characteristics are equally applicable to unloaded rubbers and to the original unvulcanized rubbers. Figure 5 gives the characteristic curve

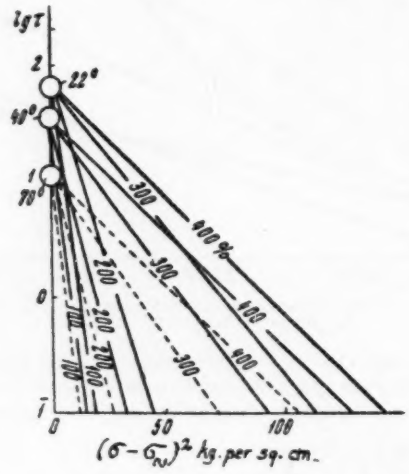

FIG. 5.—Combined graphs of relation of relaxation time to temperature, deformation, and unbalanced stress (05 rubber).

of the time of vulcanization as a function of the unbalanced stress, temperature, and elongation.

Deformation at constant rate.—The stress-strain curves for different temperatures and for different rates of deformation were plotted to ascertain the applicability of the general Equations (1) and (2) to the representation of this particular deformation system, which is more complicated than the one previously investigated. In addition, a comparison of the stress-strain curves of rubbers of varying degrees of vulcanization (obtained at a constant rate of deformation) with the corresponding equilibrium curves $\frac{d\epsilon}{dt} \to 0$ was made to verify that the relaxation properties of rubbers are independent of their state of vulcanization.

If $\frac{d\epsilon}{dt}$ = constant = ω in Equation (1), then by simple transformations we obtain:

$$\frac{d\sigma}{d\tau} = E'_0 - \frac{\sigma - E_\infty \epsilon}{\tau\omega} \tag{6}$$

Equation 6 enables us to determine experimentally the constant E'_0. From Equation 6:

$$E'_0 = \left(\frac{d\sigma}{d\epsilon}\right)_{\epsilon \to 0}$$

and the initial modulis, E'_0 can be measured by the tangent of the angle formed by a line tangent to the curve at the point $\epsilon = 0$.

As in the preceding case, the time of relaxation τ can be determined from the experimental stress-strain curves in accordance with the equation:

$$\tau = \frac{\sigma - E_\sim \epsilon}{\left(E'_0 - \frac{d\sigma}{d\epsilon}\right)\omega} \tag{7}$$

In Equation (7), for any instantaneous deformation, all the values comprising the right-hand part of the equation can be determined directly from the experimental data, as shown in Figure 6. The value of $\frac{d\sigma}{d\epsilon}$ which corresponds

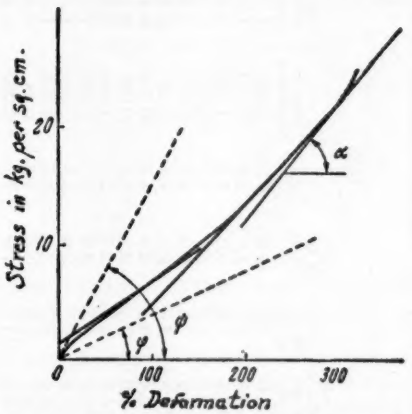

FIG. 6.—Calculation of instantaneous values of relaxation time by the stress-strain curve; temperature 70° C; $d\epsilon/d\tau = 1.65$ (for 05/20 rubber)

to the given deformation, is determined by the tangent of the angle formed by a line tangent at the appropriate point on the experimental stress-strain curve.

The times of relaxation, calculated from the experimental data according to Equation (7), can be compared with the corresponding values obtained from the experiments on stress relaxation (Figure 5). Such a comparison shows to what extent the system of deformation at any constant rate can be described by the differential Equation (1) and to what degree the relaxation properties are independent of the deformation system.

Table 2 gives the data obtained by drawing the experimental stress-strain curves at two different rates and temperatures for the 05 rubber of different degrees of vulcanization.

The graph of $\log\tau$ gives the logarithmic values of the relaxation time, calculated from the data of experiments on stretching at a constant rate given in

TABLE 2

RESULTS OF TESTS OF RUBBER STRETCHED AT A CONSTANT RATE

Mixture	Temperature (° C)	Rate of deformation in min.$^{-1}$	E'_0 in kg. per sq. cm.	$E_1 = E'_0 - E_\sim$ in kg. per sq. cm.	Deformation: 100% σ in kg. per sq. cm.	100% $\sigma - \sigma_\sim$ in kg. per sq. cm.	100% $\Delta_\sigma / \Delta_\varepsilon$	100% Log$_T$ of stretching	100% Log$_T$ of relaxation	Deformation: 200% σ in kg. per sq. cm.	200% $\sigma - \sigma_\sim$ in kg. per sq. cm.	200% $\Delta_\sigma / \Delta_\varepsilon$	200% Log$_T$ of stretching	200% Log$_T$ of relaxation
05/5	22	2.0	9.0	9.0	4.0	4.0	3.0	$\bar{1}$.548	$\bar{1}$.32	6.1	6.1	1.5	$\bar{1}$.61	$\bar{1}$.52
05/10	22	1.85	11.5	9.5	5.9	3.9	5.0	$\bar{1}$.512	$\bar{1}$.35	10.5	6.2	4.5	$\bar{1}$.68	$\bar{1}$.45
05/20	22	1.85	14.0	10.4	7.6	4.0	7.5	$\bar{1}$.528	$\bar{1}$.45	13.0	6.0	5.0	$\bar{1}$.569	$\bar{1}$.60
05/40	22	1.93	14.5	9.5	8.9	3.9	8.0	$\bar{1}$.492	$\bar{1}$.51	15.6	5.6	6.5	$\bar{1}$.562	$\bar{1}$.90
05/5	22	0.15	9.5	9.0	2.6	2.6	1.7	0.375	0.50	4.0	4.0	1.0	0.522	0.72
05/10	22	0.13	12.5	10.5	4.8	2.8	4.3	0.42	0.48	8.5	4.2	4.0	0.58	0.66
05/20	22	0.15	13.0	9.4	6.5	2.9	4.0	0.332	0.42	11.5	4.5	5.2	0.585	0.56
05/40	22	0.18	14.0	9.0	7.5	2.5	6.5	0.268	0.8	14.6	4.6	7.0	0.562	0.56
05/5	70	1.8	6.5	6.5	2.9	2.9	2.1	$\bar{1}$.564	$\bar{1}$.52	5.0	5.0	2.1	$\bar{1}$.80	$\bar{1}$.65
05/10	70	1.7	13.0	9.5	5.5	3.0	4.0	$\bar{1}$.286	$\bar{1}$.32	9.6	5.1	4.5	$\bar{1}$.54	$\bar{1}$.48
05/20	70	1.65	15.0	11.1	6.7	2.8	5.5	$\bar{1}$.244	$\bar{1}$.50	13.2	5.2	8.5	$\bar{1}$.684	$\bar{1}$.45
05/40	70	1.75	14.0	8.4	8.7	3.1	6.5	$\bar{1}$.373	$\bar{1}$.38	16.5	5.0	8.5	$\bar{1}$.716	$\bar{1}$.50
05/5	70	0.15	6.5	6.5	1.8	1.8	1.5	0.38	0.50	3.0	3.0	1.6	0.610	0.55
05/10	70	0.16	10.0	7.5	4.4	1.9	3.5	0.262	0.35	7.0	2.5	4.2	0.43	0.62
05/20	70	0.16	10.5	6.6	5.9	2.0	5.0	0.358	0.32	10.8	2.8	5.6	0.552	0.60
05/40	70	0.17	12.0	6.5	7.7	2.1	7.0	0.394	0.28	15.0	3.5	8.0	0.71	0.30

the table. The graph of $\log\tau$ (relaxation) gives the corresponding values from the graph of Figure 5 obtained from experiments on stress relaxation.

It is evident from Table 2 that in most cases there is satisfactory agreement between both values of the relaxation time. This establishes the applicability of Equations (1) and (2) to deformation at a constant rate and confirms the foregoing statement that the relaxation time is independent of the period of vulcanization.

On the other hand, a comparison of the data obtained for deformation at a constant rate with the equilibrium stress-strain curves for rubbers of different degrees of vulcanization determines the variability or invariability of the relaxation properties of a material vulcanized. In fact, at a given temperature and for a given rate of deformation, the values of the unbalanced stress are governed entirely by the relaxation properties of the material. In other words, the invariability of the $\sigma - \sigma_\sim$ values (at identical temperatures and for identical rates of deformation) during vulcanization may be another proof of the invariability of the relaxation properties.

TABLE 3

COEFFICIENT OF INTERNAL FRICTION AS A FUNCTION OF THE TIME OF VULCANIZATION

(Tests at room temperature)

Time of vulcanization at 143° C (min.)	HK		CK-1
	$\epsilon_0 = 100\%$	$\epsilon_0 = 200\%$	$\epsilon_0 = 100\%$
5	0.57	0.49	—
15	0.56	0.50	0.35
20	0.59	0.48	0.4
45	0.60	0.50	0.42
60	0.58	0.50	0.45

In this sense the independence of the relaxation properties from the vulcanization time finds sufficient confirmation in the data given in the corresponding graphs of Table 2.

As a consequence of this, and on the basis of the data in Table 2, we note that, although the stress-strain curves largely depend on the vulcanization time, the corresponding unbalanced stress-strain curves remain unchanged during vulcanization.

Spontaneous recovery.—Experiments on the measurement of the rate of spontaneous recovery give additional data supporting indirectly the conclusion as to the invariability of the relaxation properties during vulcanization. In fact, for an ideal elastic rod, the rate of motion of its end for spontaneous recovery V_T according to Equation (4) is:

$$V_T = \epsilon_0 \sqrt{\frac{E}{\rho}} \tag{8}$$

where ϵ_0 is the initial elongation; E is Young's modulus, and ρ is the density.

The existence of internal friction in real systems means that the experimentally measured rate V_e is always smaller than the theoretical rate.

$$V_e = V_T \nu \tag{9}$$

where $0 < \nu < 1$.

The coefficient ν can serve as a conventional characteristic of internal friction. The latter, for rubber, according to accepted theory, depends entirely on the relaxation properties.

With the aid of a special apparatus we measured the rate of spontaneous recovery V_s for a number of rubbers. Measuring the uniform initial deformation, the modulus, and the density of the specimens studied, we calculated[6] the coefficient ν^* according to Equations 8 and 9. This coefficient was different for vulcanizates of different rubbers, but did not change appreciably during the vulcanization of unloaded rubbers. The corresponding data for vulcanizates of natural and SK-1 rubbers are given in Table 3.

INTERPRETATION OF THE RESULTS

In the present work the relaxation properties of soft unloaded rubbers of different degrees of vulcanization (maximum time 60 minutes; optimum vulcanization 20 minutes) were studied. For five of the rubbers investigated, it was found that the relaxation properties do not change during vulcanization, within the limits of experimental accuracy. A similar conclusion follows from a comparison of the values of τ^* and β, obtained from the experiments on stress-relaxation and stretching at constant rate. This conclusion is also supported by the data obtained by comparing the dynamic stress-strain curves with the corresponding equilibrium relationships. The experiments on the rate of spontaneous recovery of rubbers of different states of vulcanization also support the same conclusion.

Inasmuch as the assumptions on which these considerations are based are not yet generally accepted and, in turn, lack further confirmation, it was interesting to verify the experimental conclusion, independently of any theoretical considerations, or according to accepted theory. By an experiment of the latter nature, we determined the hysteretic loss during dynamic deformations of constant amplitude.

In fact, since the relaxation properties studied are responsible for heat evolution, their invariability explains why the heat evolution is independent of the degree of vulcanization[7].

For the present, we have no experimental data of our own to answer this question. Data in the literature, however, agree completely with our expectations. The data of Gehman and Dillon[8] in their work on hysteresis indicate that a change of time of vulcanization within the range of 5 to 90 minutes, when the amplitude of deformation remains constant, has practically no effect on the hysteretic loss.

It is perfectly clear that the independence of the relaxation properties and the degree of vulcanization can be considered an approximation which is valid only within the limits of relatively low states of vulcanization. In particular, quite irrefutable data published by Gurevich and Kobeko[9] indicate sharp changes in the relaxation properties, which are manifest in a shift toward higher values of the temperature at which the rubber becomes glasslike, and, as vulcanization continues, finally reaches the ebonite form.

It is noteworthy, that in the formation of vulcanizates of natural and synthetic rubbers, sharp changes of the moduli E'_0 and $E_\sim$ (progressive increase in the case of SKB; curve with maximum for natural rubber)[10] are not accompanied by changes of the relaxation properties which determine the rate of establishment of equilibrium in the deformed rubber.

From the viewpoint of the theories expounded in the preceding works concerning the molecular mechanism of relaxation during high-elastic deformation, this means that, during the vulcanization of soft rubbers, the conditions which determine the reaction between the molecular chains and the nature of heat transfer do not undergo any essential changes.

Naturally, such a phenomenon can occur before the chemical bonds which are formed during vulcanization are distributed widely enough and their presence does not lead to the heat transfer by the segments of the molecular chains between these bonds. In other words, the relaxation properties of the polymer remain practically unchanged, while the middle part of the chain between the bonds of the spatial network which form during vulcanization continues to exceed in size the part of the chain which enters into heat transfer in the capacity of an independent kinetic member.

SUMMARY

1. It is shown that the process of stress relaxation at different initial elongations as well as the process of deformation at constant rate for unloaded rubbers at different temperatures (20–70° C) can be represented quantitatively by equations suggested in earlier works[3]. Likewise the possibility of expanding the theories proposed for the kinetics of high-elastic deformation of spatial polymers is substantiated.

2. It is shown that the relaxation properties of soft unloaded vulcanizates of natural rubber and many synthetic rubbers do not undergo essential changes during vulcanization.

3. The conjecture is expressed that the invariability of the relaxation properties during vulcanization continues until the bonds of the spatial network are distributed sufficiently widely not to influence the activity or heat movement of the chain segments between them.

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[5] The 06 rubbers, for which the $\log\tau^* - (1/T)$ relation is not linear in the temperature range studied, are an exception.
[6] The experiments were performed with the assistance of M. K. Khromova. The method and more detailed results will be given in a special publication.
[7] The latter statement, of course, applies only to a dynamic system with constant amplitude of deformation. In the case of unchanging amplitude of the force of deformation, the heat formation will, consequently, depend on the modulus and, naturally, will decrease with an increase of the latter during vulcanization.
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DETERMINATION OF INTRINSIC LOW STRESS PROPERTIES OF RUBBER COMPOUNDS

USE OF INCLINED PLANE TESTER *

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Physical testing methods for vulcanized natural and synthetic rubber compounds as commonly employed today do not provide an accurate basis for evaluating service performance, especially in the case of tire compounds. Poor correlation between ordinary laboratory physical tests and observed performance in tire service on the road is the rule rather than the exception.

Substantial improvement is needed in developing tests which are less subject to the human variable, tests in which the criteria examined are more in line with the actual service conditions, and tests which are mechanically simple and easy to perform. One significant advance has been made in this direction by the development of the National Bureau of Standards' comparatively new strain test[1]. This paper reports progress made by the Lee laboratories in developing one phase of an evaluation system which more accurately predicts compound performance than do the methods previously employed.

As a starting point for this work, it was decided first to determine the important physical characteristics of a tire compound and, secondly, to devise a new test or alter an existing test to give the desired information. It is assumed that an accurate appraisal of the physical characteristics listed in Table I is required.

TABLE I

PHYSICAL CHARACTERISTICS OF TIRE COMPOUNDS

Tread	Carcass
State of cure	State of cure
Dynamic energy loss	Dynamic energy loss
Rate of wear	Dynamic cord adhesion
Crack initiation and growth	Tearing resistance
Static and dynamic ozone resistance	Aging resistance
Aging resistance	
Degree of reinforcement	

HYSTERESIS LOOP TEST

The hysteresis loop test was one of the earliest tests to be used for measuring the hysteresis characteristics of vulcanized rubber[2]. It is not generally considered[3] an accurate index of hysteresis loss.

However, the hysteresis loop, measured accurately at low stress over a series of cures, does provide a remarkably accurate measure of rate and state of

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cure. Furthermore, relationship between initial load and load on recovery at low stress correlates exceptionally well with observed heat generation in actual tire service.

A 2-inch T-50 specimen is molded with a cross-section of 0.1 × 0.1 inch in the testing area. The end tabs of the specimen are 0.5 inch square and 0.1 inch thick. A series of samples is cured, for instance, for 10, 20, 40, 60, 80, and 100 minutes at 280° F. The samples are conditioned for a minimum of 16 hours at 75° F and 57 per cent relative humidity, and tested under those conditions. Tests are carried out on an IP-4 Serigraph inclined plane constant rate of load tester. The clamps used are T-50 type clamps set for a 2-inch jaw opening. A 5-pound carriage is used for tread-type compounds and a 2-pound carriage for carcass and gum-type compounds. The criteria observed are initial load, pounds per square inch at 50 per cent elongation (LI 50), load on recovery, pounds per square inch at 50 per cent elongation (LR 50), and hysteresis loss, LI 50 ÷ LR 50 or I/R 50. Loop curves are drawn automatically on a recorder chart. During the test, one end of the plane is depressed by means of a screw which travels at the rate of 22.6 inches per minute. The complete cycle for one test requires 41 seconds.

Many of these hysteresis charts have been made on natural rubber, GR-S, GR-S-10, numerous low temperature polymers, and blends of natural and polymer; numerous types of acceleration and many other variables have been tested. A very considerable amount of work has been accumulated to determine the discriminating power of this test, comparing it with a standard quick modulus test used for factory control and modulus as measured by normal stress-strain test. Duplicate evaluations have been made in comparing this test with standard stress-strain tests on many compounds. A considerable background has been established by comparing the loop test with standard stress-strain tests in the evaluation of rate of cure of natural rubber. It is used regularly as a quality control on state of cure of production batches in addition to standard quick modulus factory control tests. It will show clearly a difference in rate of cure of compounds that, at best, is only indicated in normal stress-strain results.

In the case of natural rubber, modulus follows the already established pattern of increasing through a maximum and then decreasing in value as time of vulcanization is increased. The maximum point is more clearly defined by the low stress-loop test than by standard stress-strain testing.

This test shows that the empirical hysteresis loss ratio, I/R 50, always passes through a minimum value with this minimum value; in the great majority of cases it agrees with maximum modulus, although in rare cases time to minimum hysteresis follows time to maximum modulus at slightly longer cure. This strongly indicates that hysteresis properties are closely related to modulus, but not necessarily to optimum tensile strength.

With synthetic rubber of the GR-S type, the low stress modulus increases progressively, reaching a point where the modulus change is so slight that it produces a plataeu effect. In some cases, which have not as yet been accounted for, the modulus does drop off as with natural rubber. The I/R 50 value usually passes through a minimum value, which is reached at states of cure which by other criteria are generally considered as long overcures.

The lowest cure of a series may be used as a measure of scorch accurately enough for practical factory control. Table II shows the type of data obtained.

TABLE II

EFFECT OF TIME OF CURE

Cure (min. at 280° F)	Case A			Case B		
	LI-50	LR-50	I/R-50	LI-50	LR-50	I/R-50
10	86	—	—	74	—	—
20	129	60	2.15	116	43	2.70
40	159	83	1.92	147	76	1.94
60	154	74	2.08	157	83	1.89
80	145	65	2.24	157	82	1.89
100	140	60	2.33	156	81	1.93

These data represent two types of acceleration in a crude rubber tread compound with 50 pounds per hundred of rubber loading of a blend of high abrasion furnace and fine furnace blacks. The readings are in pounds per square inch.

In case A, the compound develops its maximum modulus at approximately 40 minutes, and also at this point the measure of hysteresis loss has reached a minimum, followed by a definite drop in modulus and rise in hysteresis loss ratio at longer cure. In case B, the maximum modulus and minimum hysteresis ratio are reached in approximately 60 minutes and show only a slight change at 100 minutes.

The authors' interpretation of the data is that, in case A, optimum hysteresis properties have been reached at approximately 40 minutes and, in case B, at approximately 60 minutes.

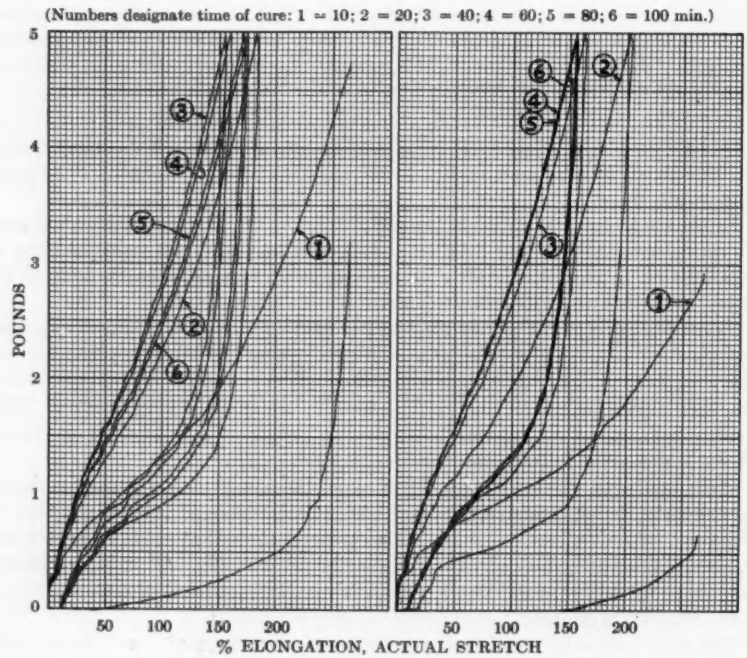

FIG. 1.—Test charts. *Left.* Case A. *Right.* Case B.

The hysteresis loss of case A in 40 minutes is approximately equal to that of case B in 60 minutes, showing equivalent heat build-up properties for the two stocks at their own respective time levels.

The accelerator in case A develops a somewhat peaky cure curve with respect to both modulus and hysteresis change with time of cure, whereas the accelerator used in case B develops more of a plateau effect.

The modulus level of both compounds is similar.

Finally, because of its lower 10-minute modulus level, B is less scorchy than A. It may be noted in Table VI and Figure 4 that a compound containing benzothiazyl disulfide is more scorchy than the one containing mercaptobenzothiazole. The disulfide is not normally considered as scorchy as the thiazole, but unexplained reversals have been experienced in the factory on occasion with high-abrasion and high-modulus furnace types of black.

Because the correlation between conventional tensile testing and road testing is questionable, and heat generation is one of the most important factors to consider in tire development, the loop test provides a good keystone for an evaluation system. The minimum hysteresis point is clearly defined in the case of natural rubber. However, in an analysis of synthetic-rubber compounds, judgment must be used in selecting the proper cure, for in most cases there is no minimum point. It would appear from the work so far that the point to be selected is the beginning of the modulus plateau.

The phenomenon of modulus passing through a maximum and then decreasing, which occurs always in natural rubber and occasionally in GR-S types, is difficult to resolve.

If we assume chemical cross-linkage to be the result of vulcanization, these data would indicate that with vulcanization carried into the range of what is by normal concept overcure, there is some breakdown of the cross-linkage structure formed in the early part of the cure in the case of natural rubber.

A comparison of the data on natural rubber and GR-S could also be interpreted to show either a difference in the type of cross-linkage or a more stable linkage formed in the case of GR-S, or a combination of both.

Figure 1, a reproduction of the actual test charts for these two sets of data, serves to illustrate graphically the points referred to in Table II. The waviness of the lines does not represent the result of inertia in the testing apparatus. It is apparently related to resilience, *i.e.*, a more resilient rubber compound shows a greater degree of waviness than does a synthetic rubber compound of less resilience. The waviness increases in the same compound with increased state of cure. Actual values from wavy portions of the curve are normally taken using a French curve to determine the mean of the waviness. Also, in normal practice, only three tests are made per chart to improve accuracy in reading. All six cures are given in Figure 1 to show the continuity of the cure curves over the entire series.

This test is extremely accurate and reproducible and is not subject to the human error found in the standard stress-strain curve. Samples are rejected for this test if they do not conform to limits of ± 0.003 inch in sectional dimension, and all samples are inspected for molding defects.

A statistical analysis is shown in Table III of 25 samples of a natural-rubber tread compound tested by this method.

Observations have indicated that the stiffness relationship among several compounds varies, depending on whether the measurement is made at extremely low elongation or at the more conventional 300 per cent modulus. The data in Table IV compare modulus from hysteresis loop measurements at

TABLE III

STATISTICAL ANALYSES OF NATURAL RUBBER TREAD COMPOUND

	LI 50	LR 50
Av. $\bar{X}$ (lb./sq. inch)	215.2	101.84
Maximum (lb./sq. inch)	221	110
Minimum (lb./sq. inch)	206	97
Standard deviation (σ)	13.72	3.16

25, 50, and 100 per cent elongation with corresponding measurements at 100 and 300 per cent modulus, made on a Scott L-5 tester. The samples were cut from a group of 9.00–20 10-ply highway tires which had been road-tested for approximately 20,000 miles.

Seven different trends were included in this test; the main variable was the rubber hydrocarbon used, but there were slight variables in amount of plasticizer and accelerator. The numbers in parentheses following each load measurement indicate the relative order of stiffness; 1 is the stiffest compound. Stiffness relationship is the same at 25 and 50 per cent modulus, and at 100 percent changes in order are observed. At 300 per cent modulus, six of the treads are grouped together within a 275 pounds per square inch spread and the seventh is somewhat softer.

TABLE IV

MEASUREMENT OF MODULUS

	Hydrocarbon	Hysteresis loop			Standard	
		L25%	L50%	L100%	L100%	L300%
A	GR-S-10	122(7)	186(7)	386(6)	400	2150(7)
B	Natural	128(6)	192(6)	372(7)	400	2500(5)
C	X-485	183(1)	262(1)	491(1)	450	2650(2)
D	X-478	170(2)	245(2)	412(5)	485	2500(4)
E	GR-S-10-natural	148(5)	226(5)	487(2)	525	2400(6)
F	X-485-natural	153(4)	230(4)	457(4)	500	2625(3)
G	X-478-natural	156(3)	235(3)	458(3)	500	2675(1)

Because the actual stress on a tire tread in service is more closely related to modulus at 25 to 50 per cent than to modulus at 300 per cent, the criteria observed at low modulus are believed to be more nearly representative. Low modulus measurements agree far better with observed hardness.

TABLE V

RELATION OF HYSTERESIS LOSS AND TEMPERATURE

	GR-S-10	Crude	X-485	X-478	GR-S-10/ Natural	X-485/ Natural	X-478/ Natural
I/R 50 hysteresis loss	2.64	1.86	2.47	2.53	2.34	2.26	2.42
Goodrich Flexometer (ΔT° F)	41	30	38	41	32	26	26
Tire temp. (ΔT° F)	117	96	111	113	109	109	109

On the same series of treads, a comparison was made between I/R 50 hysteresis loss, ΔT measured by Goodrich flexometer, and actual tire temperature. The agreement between ΔT as measured by the Goodrich flexometer and actual tire temperature was not particularly good. The heat build-up on the part natural-part X-478 and the similar compound with X-485 was 4° F lower than the all-natural compounds, whereas the actual tire temperatures of both compounds were 13° F above the natural rubber. The agreement between I/R

TABLE VI

EFFECT OF ACCELERATOR VARIABLES

	Accelerator									
	1	2	3	4	5	6	7	8	9	10
N-Cyclohexyl-2-benzothiazole sulfinamide	0.35	0.25	—	—	—	—	0.25	0.30	0.20	0.15
Ureka base[a]	—	0.50	—	—	—	—	—	—	—	—
Benzothiazyl disulfide	—	—	0.50	—	—	—	—	—	—	—
Mercaptobenzothiazole	—	—	—	0.40	—	—	—	—	0.15	0.20
2-Benzothiazyl-*N*,*N*-diethylthiocarbamyl sulfide	—	—	—	—	0.20	—	—	—	—	—
Amax[b]	—	—	—	—	—	0.40	—	—	—	—
Ridacto[c]	—	—	—	—	—	—	0.25	—	—	—
Diphenylguanidine	—	—	—	—	—	—	0.10	—	—	—
Normal lead salicylate	—	—	—	—	—	—	—	0.30	—	—

[a] Not disclosed by manufacturer.
[b] Retarded benzothiazyl type.
[c] Amine soap.

50 hysteresis loss and tire temperature was considerably better, as shown in Table V. Goodrich measurements were made under the following conditions: stroke 0.175, load 24 pounds 4 ounces, oven 212° F.

A natural-rubber tread compound reinforced with high-abrasion furnace and fine furnace blacks was tested with ten accelerator variables. These vari-

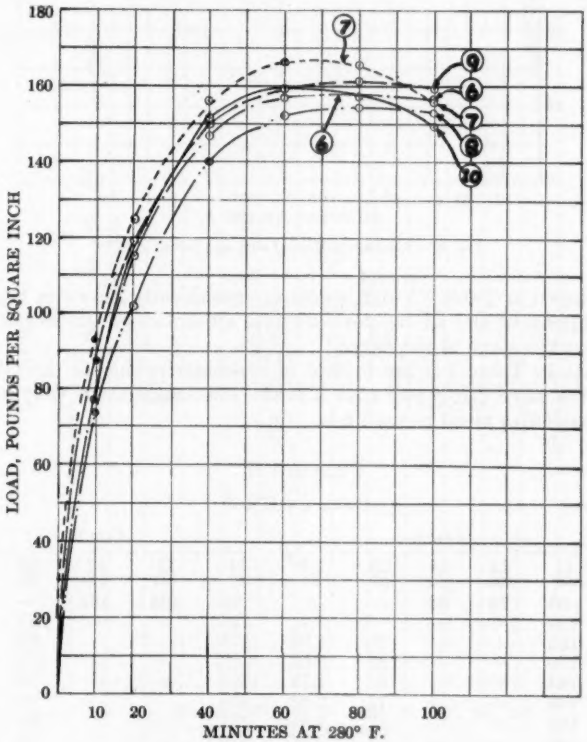

FIG. 2.—Relation of time of cure and initial load.

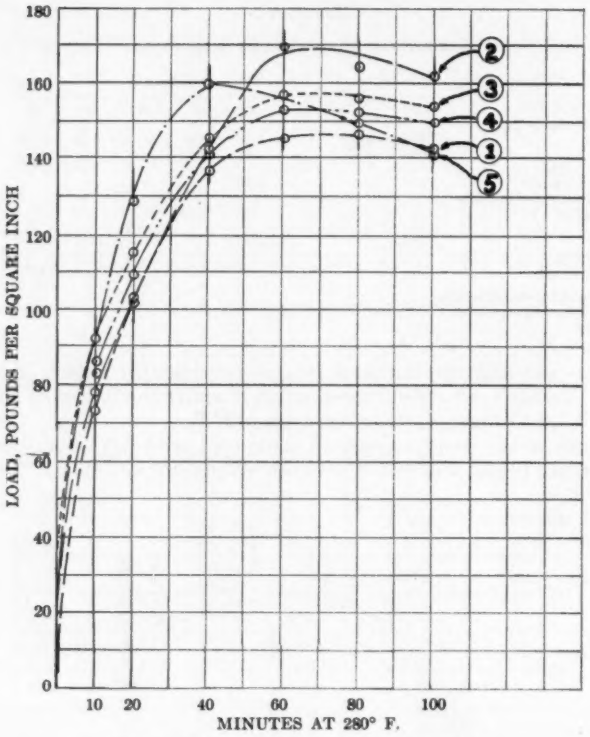

FIG. 3.—Relation of time of cure and initial load.

ables are shown in Table VI and results are graphically shown in Figures 2 to 5. LI 100 per cent and LI 150 per cent data are shown on the scorch cure only to determine the slope of the curve.

The data in Table VII are typical of synthetic rubber of the GR-S type. Case A is standard GR-S and case B is the low temperature polymer X-478. Both are passenger tread compounds.

TABLE VII

DATA ON GR-S

	Case A					Case B				
Cure (min.)	LI 50	LI 100	LI 150	LR 50	I/R 50	LI 50	LI 100	LI 150	LR 50	I/R 50
10	56	76	83	—	—	93	128	162	—	—
20	109	—	—	—	—	145	—	—	53	2.74
40	136	—	—	28	4.86	175	—	—	66	2.64
60	170	—	—	55	3.09	185	—	—	75	2.45
80	183	—	—	67	2.73	194	—	—	90	2.16
100	186	—	—	71	2.62	198	—	—	94	2.11
120	188	—	—	72	2.61	201	—	—	95	2.10
140	190	—	—	74	2.57	199	—	—	93	2.16
160	195	—	—	75	2.60	199	—	—	91	2.19

TABLE VIII

COMPARISON OF TIRE CURE AND LABORATORY PRESS CURE

Cure (min. at 280° F)	Tubed tread			Tire section		
	LI 50	LR 50	I/R 50	LI 50	LR 50	I/R 50
10	—	No cure		—	—	—
20	98	—	—	—	—	—
40	150	51	2.94	154	59	2.61
60	169	77	2.19	—	—	—
80	182	93	1.96	—	—	—
100	179	90	1.99	—	—	—

This illustrates the greater hysteresis loss of standard GR-S when compared to low temperature polymer X-478. The spread between maximum initial modulus is considerably less than the spread at maximum modulus on recovery. There is only a 6-pound differential between GR-S and X-478, with X-478 the higher of the two, whereas the GR-S is 20 pounds lower on recovered load. This is true in spite of the fact that the black loading on the polymer hydrocarbon was 10 per cent higher in the case of the X-478 stock. The minimum hysteresis loss ratio was 2.57 for GR-S as compared to 2.10 for X-478.

The hysteresis loop provides a very accurate means of comparing tire cure

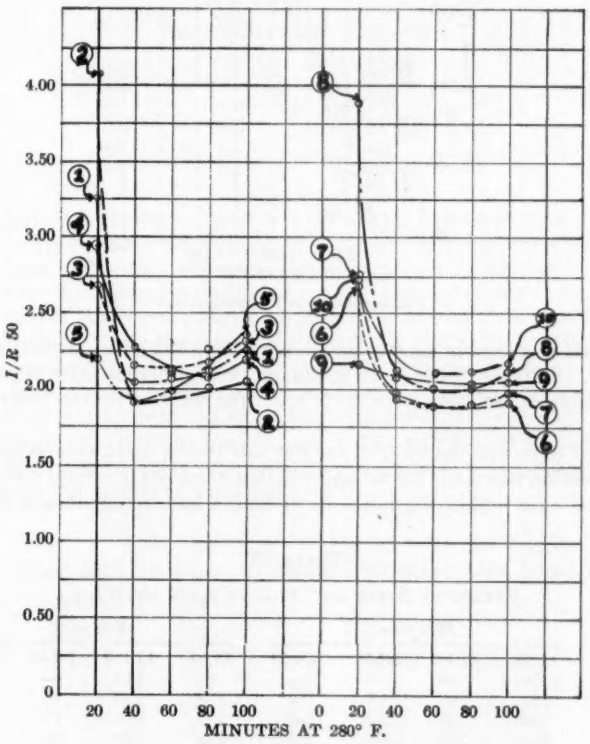

FIG. 4.—Relation of hysteresis and time of cure.

with laboratory press cure. The data in Table VIII compare a specimen cut from the tread of a freshly cured tire to the laboratory press cured series on the tubed tread compound.

The data on the tire section indicate an equivalent cure of about 45 minutes at 280° F.

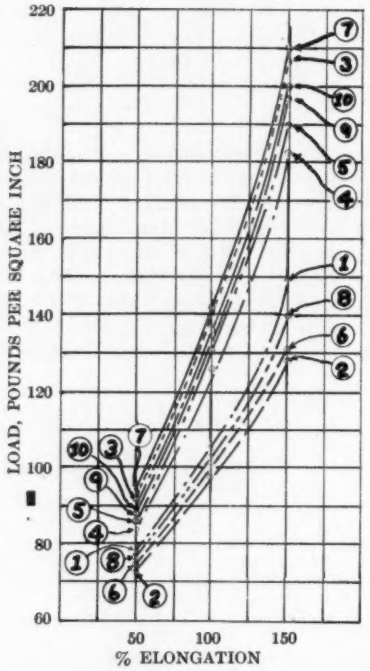

FIG. 5.—Scorch at 10-minute cure.

This test was used in an attempt to determine the effect of state of cure on road wear. Batches of the same compound with different rates of cure due to possible polymer variation were made into tires, which were road-tested on two test cars.

State of cure was determined on the tire treads upon completion of test. After correction was made for car and weather variables, the data indicated that the state of cure within the range investigated had no significant bearing on

TABLE IX

EFFECT OF STATE OF CURE ON RATE OF WEAR

Cure (min. at 280° F)	Slow cure				Fast cure			
	LI 50	LI 100	LR 50	I/R 50	LI 50	LI 100	LR 50	I/R 50
20	76	98	—	—	89	113	—	—
40	121	167	—	—	138	210	25	5.52
60	156	237	58	2.69	187	291	77	2.43
80	161	252	66	2.44	198	329	89	2.22
100	161	260	66	2.44	187	316	86	2.18

rate of wear. The results on the press-cured slabs are shown in Table IX and in Table X a comparison of hysteresis loop and milage is given.

TABLE X

COMPARISON OF HYSTERESIS LOOP AND MILAGE

	Tire sections			Wear, Miles/0.001
	LI 50	LR 50	I/R 50	
Fast	203	105	1.94	80
	202	95	2.13	89
	196	85	2.30	86
	180	80	2.25	94
Slow	180	69	2.62	83
	177	70	2.53	92
	171	68	2.52	80
	171	63	2.72	78

The hysteresis loop data in Table XI illustrate the use of this test as a means of evaluating state of cure of natural rubber. Time to maximum modulus at low strain is shown for three lots of smoked sheets compounded in the ACS I rubber test recipe.

TABLE XI

TIME TO MAXIMUM MODULUS

Lot	Time to Max. Mod. at 280° F, Min.	LI 50	LR 50	I/R 50	Set, %
1	60	55	48	1.15	5
2	60	61	54	1.13	2
3	40	62	56	1.11	2

A comparison is shown in Table XII of tests on five bales from a single lot of natural rubber tested according to the standard stress-strain and by the hysteresis loop. The standard stress-strain test shows a considerable variation in rate of cure which was not evident in the loop test. Factory experience with this lot of rubber in tire compounds indicated that it was more correctly evaluated by the loop than by the standard stress-strain test. It could be predicted from the loop test that the factory control cure tests on the mixed compound would be fairly uniform and within specifications. Based on the standard 600% modulus test, some of the mixed compound would be expected to be outside the cure specifications on the high side with a substantial variation in rate of cure. The actual results were fairly uniform and average rate of cure fell slightly above the middle of the specifications.

TABLE XII

COMPARISON OF STANDARD STRESS–STRAIN AND LOOP TESTS

Sample	Standard test, Mod. at 600% – 40 at 260° F	Time to max. LI 50 at 280° F, Min.	LI 50	LR 50	I/R 50	Set, %
1	525	40	68	51	1.33	5
2	1300	40	77	64	1.20	3
3	675	40	76	60	1.27	5
4	1050	40	69	55	1.25	5
5	500	40	70	57	1.23	4

The authors concur with the recent report of the British Rubber Producers' Research Association[4] that evaluation of natural rubber for state of cure should be made at modulus under 250% elongation.

The loop test has been adopted by this laboratory as an integral part of a revised evaluation system for compounds. In the operation of the revised system, the loop test is made and cures for the remaining tests are determined from the results.

CONCLUSIONS

A hysteresis loop test made at low stress over a series of cures provides an extremely accurate measure of state of cure.

The test is accurate and reproducible when made on test pieces which have been conditioned and are tested under controlled conditions of temperature and relative humidity. Furthermore, the type of test machine used and the autographic recording of the data practically eliminate the human element in testing.

The accurate molding of the test pieces eliminates possibilities of error in gaging and compensating found frequently in the standard stress-strain test.

The initial load data at 50, 100, and 150% elongation on the shortest cure in the series provide a scorch test which is accurate enough for practical factory control.

The ratio of initial modulus at 50% elongation to modulus on recovery at 50% elongation provides a measure of hysteresis loss or heat build-up.

Measurements made in the range of 50% elongation appear to be a more accurate measure of the properties of tire stocks, because the test range more closely approaches the conditions under which tire stocks operate in service.

Finally, the use of this test provides a considerable saving in testing time.

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DYNAMIC PROPERTIES OF RAW AND VULCANIZED POLYMERS *

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Observation of raw polymer elasticity appears probable in view of a suggestion made in 1831 by Poisson that even liquids exhibit shear elasticity with high velocity deformation[1]. This idea was based on experience with materials, such as pitch, which respond elastically to a sharp blow but flow under heavy loads of long duration. The familiar mechanical model of Maxwell[2], consisting of a spring and dashpot in series, was devised to give a physical picture and permit mathematical formulation for this viscoelastic type behavior.

If such a model is subjected to a low-frequency sinusoidal force, the response is similar to that of a viscous liquid. At high frequencies, however, the shear elasticity term is predominant.

It is apparent that the frequency range in which each type behavior is manifest varies widely for different materials, and depends roughly on the ratio of viscosity to shear modulus. The elastic response which can be secured from polymer solutions, liquid polymers, and polyisobutylene had been investigated rather extensively in recent years, especially by Ferry and coworkers[3], who used electromagnetic transducers covering a frequency range of about 20 to 1000 cp. and Mason[4] using shear waves generated by piezoelectric crystals in a frequency range of from about 16 kc, per second to 60 mc. per second. Nolle[5] has recently published results of extensive investigations on the dynamic properties of vulcanized rubber.

There seems to have been no application of the above methods to testing and studying raw polymers, such as butadiene copolymers, of particular interest in synthetic rubber development. The information available from published work made it probable that an elastic response could be secured from raw polymers in the audiofrequency range. Especial interest lies in the possibility of using such data for evaluating the elastic quality of raw polymers if the measurements can be made rapidly and accurately on small samples, such as result from bottle polymerizations. The response to alternating deformations is one of the most critical measurements of the essential rubberlike nature of a polymer. Plasticity measurements, on the other hand, emphasize the flow properties. The extent of the persistence of the elastic properties of the raw polymer in vulcanized compounds is a fascinating and potentially useful objective for dynamic studies on raw polymers.

EXPERIMENTAL METHOD

It was found that the Goodyear Vibrotester could readily be adapted for dynamic measurements of raw polymers, the only changes required being in the

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type of test-piece and its mounting. The Vibrotester includes an electromagnetic type transducer which is tuned to resonance for the dynamic measurement. Details of the apparatus and operating procedure have already been published[6]. The resonance frequency chosen for raw polymer measurements was in the vicinity of 60 cycles per second. It was measured in each case to about one fourth of a cycle by means of a vibrating reed frequency meter. The resonance vibration amplitude was maintained constant in all tests to eliminate variations of dynamic properties with amplitude.

One of the principal problems encountered in making dynamic measurements on raw polymers was that of securing a test-piece of exact geometrical reproducibility, free of air bubbles, and one which could be prepared in a reasonable time.

A satisfactory solution was achieved by molding the polymer between two concentric brass cylinders. A sketch of the test-piece is shown in Figure 1*A*.

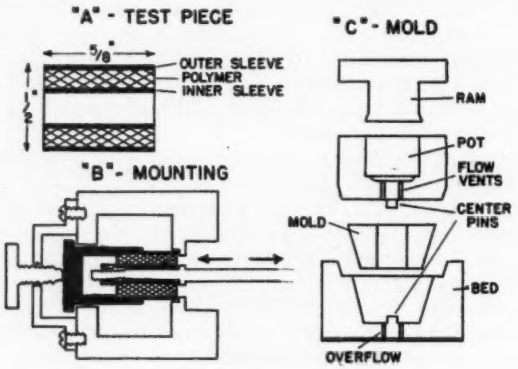

FIG. 1.—Test-piece and mold.

The dimensions were chosen to give a resonance response within the range of the Vibrotester and to permit mounting of the test-piece in the apparatus by means of fittings readily interchangeable with those ordinarily used in measuring vulcanized compounds under compressive vibrations.

The polymer dimensions in the test-piece are $\frac{5}{8}$ inch long, $\frac{7}{16}$ inch outside diameter, and $\frac{1}{4}$ inch inside diameter. Figure 1 includes a sketch (*B*) indicative of the way in which the test-piece is mounted in the Vibrotester. The outer sleeve is clamped and the inner sleeve is vibrated axially. The resonance frequency is determined by the axial stiffness or spring rate of the test-piece and the mass of the vibrating system according to the relation:

$$\text{Spring rate (dynes/cm.)} = Mp^2 \tag{1}$$

where M = mass (grams) of the vibrating system and p = radian frequency ($2\pi f$) at resonance.

The shear modulus is related to the spring rate by the following equation:

$$\text{Spring rate (dynes/cm.)} = \frac{2\pi SL}{2.3 \log \frac{R_0}{R_1}} \tag{2}$$

where S = shear modulus (dynes per sq. cm.); L = length (cm.); R_0 = outer radius of polymer; and R_1 = inner radius of polymer.

Introduction of the test-piece dimensions and the proper conversion factors in Equations 1 and 2 gives, at 60 cycles per second:

$$S \text{ (kg. per sq. cm.)} = 0.00813\ M$$

The internal friction, η, is given by:

$$\eta = b\left(\frac{2.3}{2\pi L}\log\frac{R_0}{R_1}\right) \tag{3}$$

b = proportionality factor between frictional force and velocity (dynes per cm. per second).

In practice, η is obtained by use of the following relation which introduces the force calibration constant and amplitude magnification factor of the instrument:

$$\eta \text{ (kilopoises)} = 10.17\frac{I}{T} \tag{4}$$

where I = driving current at resonance (amperes), 60 cycles, and T = length of amplitude trace (cm.).

The resilience is given by:

$$R\ (\%) = 100e^{-2.41\eta/S} \tag{5}$$

where η is in kilopoises and S in kg. per sq. cm.

The linear amplitude of the vibrating system was ± 0.0182 cm. corresponding to a shear strain amplitude of ± 0.0764 radians or 4° 23 minutes.

A sketch of the transfer-type mold used in forming the test-samples is shown in Figure 1*C*. Although not entirely satisfactory, it has, in general, given raw polymer test-pieces of good reproducibility when they were not obviously defective.

It is necessary to prepare the metal surfaces of the test-piece to obtain polymer adhesion. In the case of raw polymers, painting such surfaces with a thin coat of Pliolite was found adequate. For vulcanized samples, Ty-Ply adhesive was used.

In forming the sample, the mold and test cylinders are first heated to approximately 290° F. The raw material is then loaded and the transfer molding completed, followed by a heating period of about 1 minute to allow for polymer expansion. The test-piece is then cooled while in the mold to room temperature or below.

The Vibrotester was originally designed to use two vulcanized test-pieces, 0.5 inch in diameter and 0.5 inch high. These were subjected to 8 per cent static compression, on which was superposed the compressive oscillations. This procedure is not suitable for raw polymers. The tubular test-piece which was developed for raw polymers could also be used for vulcanized samples, but care was required with the rubber-metal adhesion. Shrinkage on cooling after vulcanization sometimes gave trouble in securing good adhesion, especially with the gum stocks of some of the polymers studied. For this reason, many of the comparisons of dynamic properties of vulcanizates were made with the regular compression type of test-piece. It is probable that a flat test-piece with rubber sandwiched between two metal plates would be more universal in its adaptation for both raw and vulcanized polymers.

POLYMERS AND COMPOUNDS USED

Polymers furnished by the Government laboratories were used in this work. Information furnished on these polymers is reproduced in Table I.

Table II shows the compounds used in preparing gum stocks of these polymers.

In addition, some stocks were prepared using the formulas in Table III.

To supplement the raw polymers furnished by the Government laboratory, two series of butadiene-styrene copolymers were prepared in the Goodyear laboratory. These were made with butadiene styrene charging ratios of 100/0, 90/10, 80/20, 70/30, and 60/40 using polymerization temperatures of 122° and 41° F. In addition, sodium polybutadiene, high and low temperature polyisoprene polymers, and a series of copolymers of butadiene with ethyl acrylate and butyl methacrylate were prepared for this work.

TABLE I

POLYMERIZATION DATA

Sample no.	Polymerization temp. (° F)	Hydrocarbon conversion (%)	Raw Mooney viscosity (212° F) ML-4
	GR-S, temperature variations		
1	122	61	61
2	41	60	60
3	14	59	58
	GR-S, conversion variations		
4	122	42	54
5	122	55	53
6	122	72	48
7	122	75	39
8	122	100	43
	GR-S, Mooney viscosity variation (compare with samples 6 and 7)		
9	122	73	60
	Polyisoprene samples		
10	131	58	48
11	131	42	47
12	41	58	43

TABLE II

COMPOUNDS USED

(Cure, 120 minutes at 290° F)

Sample no.	1	2	3	4	5	6	7	8	9	10	11	12	Hevea
	Parts												
Polymer	100	100	100	100	100	100	100	100	100	100	100	100	100
Softener	5	5	5	5	5	5	5	5	5	5	5	5	5
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Sulfur	2	2	2	2	2	2	2	1.5	2	2	2	2	2.25
Mercaptobenzothiazole	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.0
Stearic acid	—	1.5	—	—	—	—	—	—	—	—	—	—	3.0
25% Diphenylguanidine masterbatch	—	0.8	—	—	—	—	—	—	—	—	—	—	—

TABLE III

ADDITIONAL COMPOUNDS

(Cure at 290° F: A, 120 min.; B and C, 90 min.)

	A	B	C
	Parts		
Polymer	100	100	100
Zinc oxide	5	5	5
Sulfur	2.5	2	2
Mercaptobenzothiazole	1.5	—	—
N-cyclohexyl-2-benzothiazole sulfenamide	—	1	1
Stearic acid	1	2	2
Paraflux	—	5	5
Phenyl-β-naphthylamine	1	—	—
Agerite HiPar	—	1	1
Easy processing carbon black	—	—	10, 20, or 40

Goodyear production polymers were used in observing the effect of Mooney plasticity on dynamic measurements.

RESULTS

To determine the overall reproducibility of the method, five test-pieces of polymer 9 were prepared and measured. The results were as follows:

Test piece	*S*, kg./sq. cm.	η, kilopoises	*R*, %
1	6.72	3.00	34.3
2	6.60	2.84	35.5
3	6.72	3.00	34.2
4	6.38	2.80	34.8
5	6.38	2.84	34.2
Av. deviation from mean, %	2.1	2.9	1.3

This degree of reproducibility seems to compare favorably with that secured in other methods of rubber testing.

A study was made of the effect of plasticity on the dynamic measurements. To do this, Goodyear production polymers, X-520 and X-509 (cold rubbers) and X-361 (GR-S) were milled for different lengths of time to provide a series of samples having Mooney plasticities from about 70 to 35. The resilience values determined for these samples are plotted in Figure 2. The resilience is char-

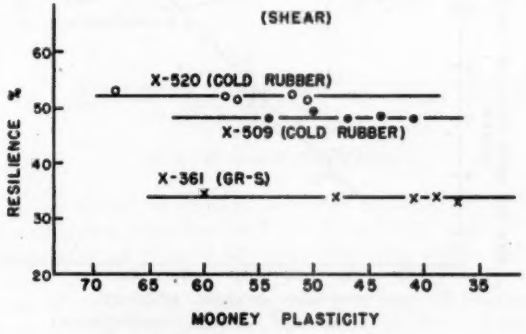

FIG. 2.—Mooney plasticity vs. resilience.

acteristic of the polymer and independent of its Mooney plasticity. The dynamic modulus and internal friction were also constant for any one of the polymers within the limits of experimental error for this range of Mooney plasticity.

Relatively long relaxation times associated with the molecule as a whole are effective for determining the Mooney plasticity as evidenced by its dependence on molecular weight. The dynamic measurements, on the other hand, are

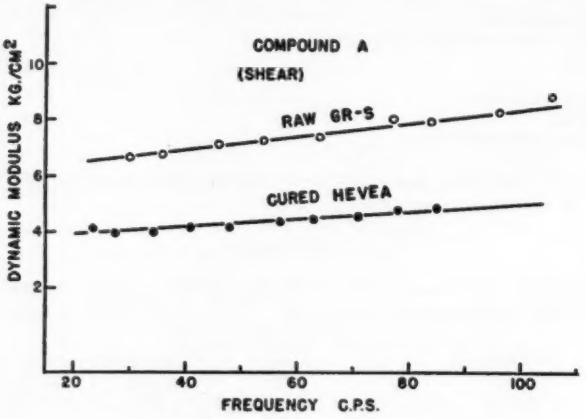

FIG. 3.—Dynamic modulus vs. frequency.

probably influenced primarily by shorter relaxation times associated with smaller units of structure, such as segments of the molecules. Figure 3 gives plots of dynamic modulus versus frequency for a raw production GR-S gum stock and a cured Hevea gum stock; these illustrate the extent of the dependence of modulus on frequency under the test conditions.

It is reasonable to suppose that the molecular structural elements which determine the dynamic properties of a raw polymer tend to persist and deter-

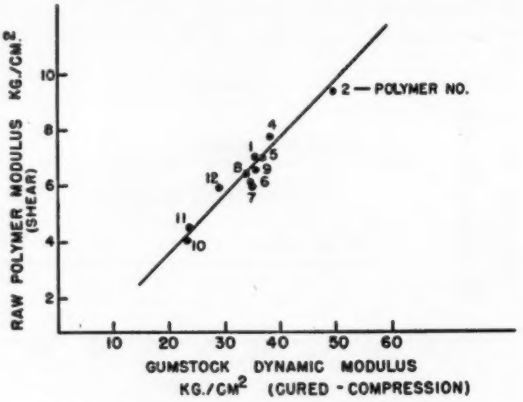

FIG. 4.—Modulus correlation for raw and cured polymers.

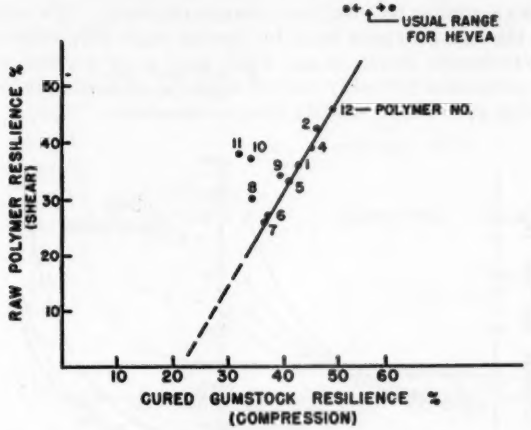

FIG. 5.—Resilience correlation for raw and cured polymers.

mine these properties in a vulcanizate of the polymer. Vulcanization, which is primarily the formation of a rather large network structure of cross-linkages, suppresses the type of plastic flow to which dynamic measurements have been shown to be insensitive. There should, therefore, be at least a broad correlation between the dynamic properties of raw polymers and similar vulcanizates prepared from them. The dynamic properties are of course, influenced by the

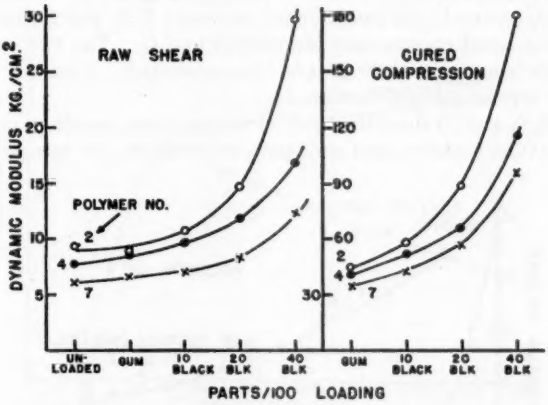

FIG. 6.—Effect of loading on modulus.

compounding and extent of cure, so an exact correspondence between values for raw and vulcanized polymers is not to be expected. As shown later, however, the dependence on state of cure soon reaches a rather flat plateau as the cure progresses.

Figure 4 shows the extent of the correlation observed between the dynamic modulus measured for the raw polymers listed in Table I and the dynamic modulus for corresponding vulcanizates compounded according to Table II.

Figure 5 shows a similar plot for the dynamic resilience. The dynamic measurements on the raw polymers seem to disclose basic properties which are inherent in the molecular structure and which tend to persist through vulcanization. These properties probably control what can be accomplished in the way of compounding good elastic quality into a vulcanizate.

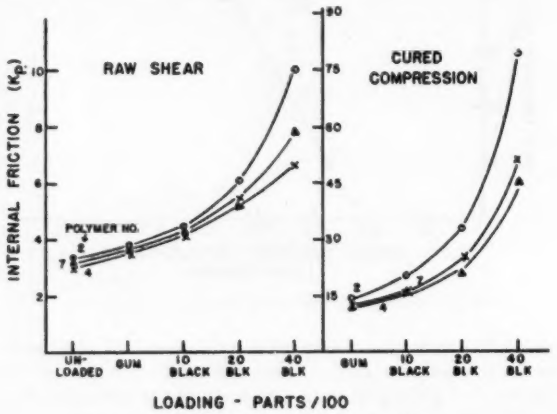

FIG. 7.—Effect of loading on internal friction.

Figure 6 shows the effect of carbon black loadings on the dynamic modulus for unloaded, uncured, but compounded polymers 2, 4, and 7 and also for the corresponding cured compounds, formulas B and C. The two sets of curves are strikingly similar in their general characteristics. Figure 7 is the same type of plot for the internal friction.

Figures 8, 9, and 10 show the effect of temperature variation on the internal friction, dynamic modulus, and resilience, respectively, for raw polymer 4 and

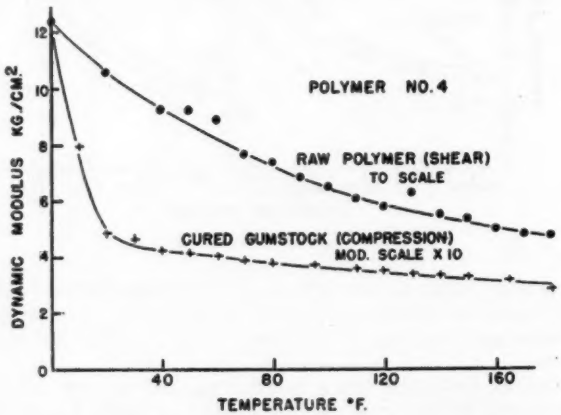

FIG. 8.—Effect of temperature on modulus.

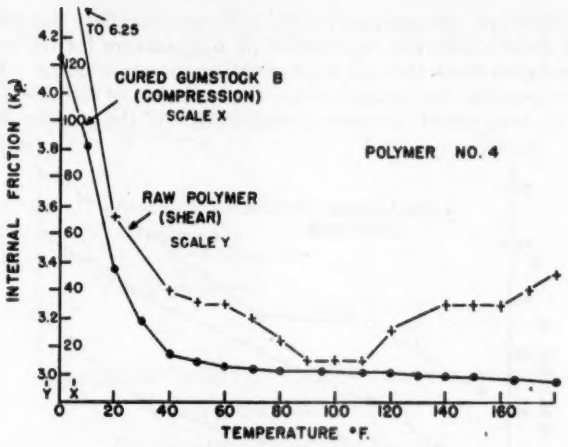

FIG. 9.—Effect of temperature on internal friction.

its cured gum stock. The dynamic modulus decreases with increase in temperature, indicating that the molecular configuration mechanism for rubberlike elasticity is not controlling in this case; more probably a relaxation mechanism dominates. The dynamic modulus for the cured gum stock shows a much greater sensitivity to temperature at the low temperature end of the curve than does the raw polymer. The measurements at the lower temperatures evidently

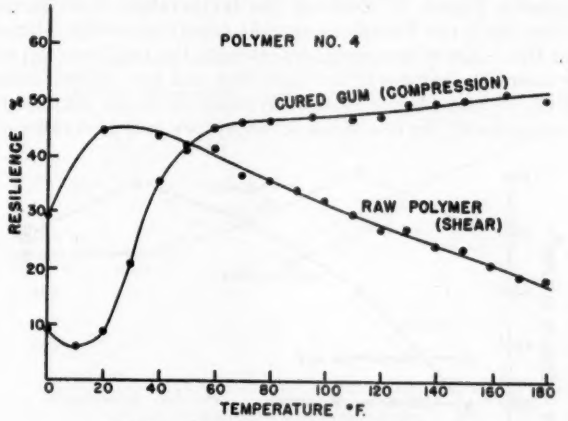

FIG. 10.—Effect of temperature on resilience.

bring into prominence differences in the relaxation spectra for the raw polymer and the vulcanizate.

On the other hand, curves of internal friction *vs.* temperature (Figure 8) tend to deviate at the high temperature end of the curve, where the relaxation periods for the raw polymer may become so reduced that larger molecular segments become mobile at the frequency used, and losses essentially due to plastic flow occur.

The resilience *vs.* temperature curves in Figure 10 reflect the effect of these factors and show a different dependence on temperature for the raw polymer and the cured gum stock through most of the temperature range. Throughout the high temperature end of the range, the resilience of the raw polymer decreases as the temperature increases, whereas that of the cured gum stock improves.

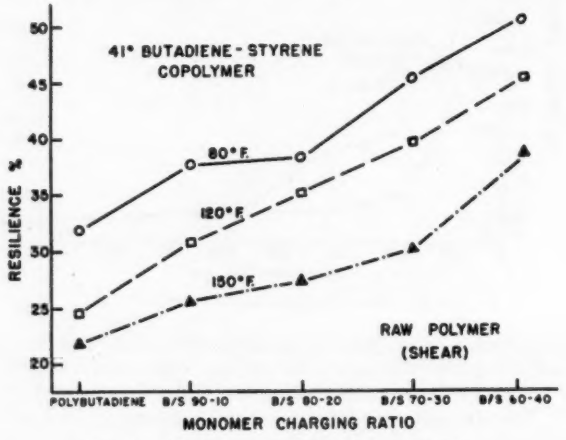

FIG. 11.—Effect of temperature with charging ratio.

The curves in Figure 11 illustrate the temperature dependence of the resilience for a series of raw butadiene-styrene copolymers with different charging ratios. For the range of temperatures studied, the resilience depends on temperature in about the same way for both high and low styrene ratios.

Figures 12, 13, and 14 give plots of dynamic modulus, internal friction, and resilience, respectively, for two series of laboratory prepared raw polymers with

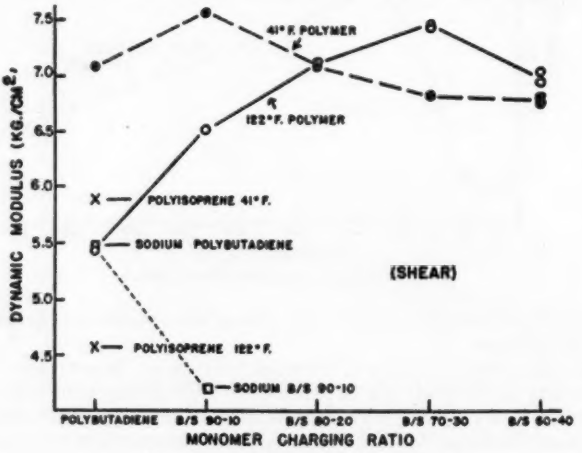

FIG. 12.—Modulus *vs.* charging ratio.

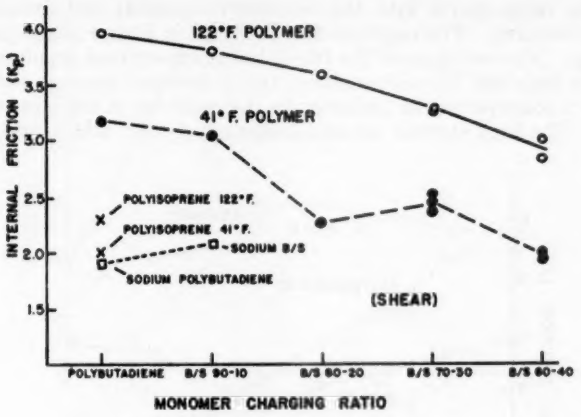

FIG. 13.—Internal friction vs. charging ratio.

variable charging ratios of butadiene and styrene and polymerization temperatures of 41° and 122° F.

The 41° F polymers are characterized by lower internal friction and higher resilience than the corresponding 122° F polymers. The points entered on the graphs for polyisoprene and sodium polybutadiene show that these polymers have very low internal friction and improved resilience. The polyisoprene

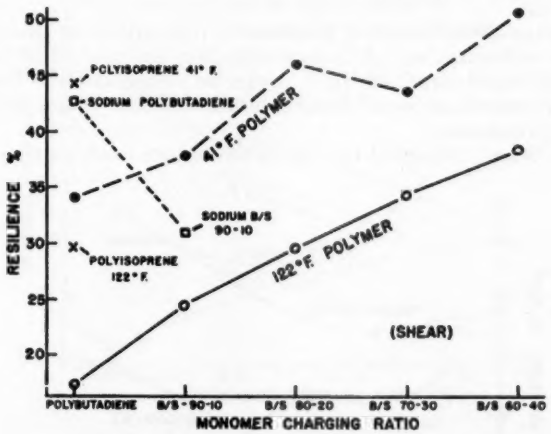

FIG. 14.—Resilience vs. charging ratio.

polymer prepared at 41° has significantly improved dynamic properties over that prepared at 122° F. The dynamic properties of the 41° F polyisoprene polymer compare favorably with the sodium polybutadiene polymer.

Figures 15, 16, and 17 give plots of internal friction, dynamic modulus, and resilience, respectively, against curing time for polybutadiene, 60/40 butadiene-styrene copolymer, and Hevea gum stocks. Compound formula A was used.

The curing range starts with the uncured compounds and extends to pronounced overcures. The resilience trends shown in Figure 17 are particularly interesting. The resilience of the 60/40 butadiene-styrene copolymer is initially higher than that of polybutadiene, but it does not improve so much with cure. As a consequence, at higher cures the resilience of the polybutadiene is superior. The high styrene content of the copolymer, which does not enter

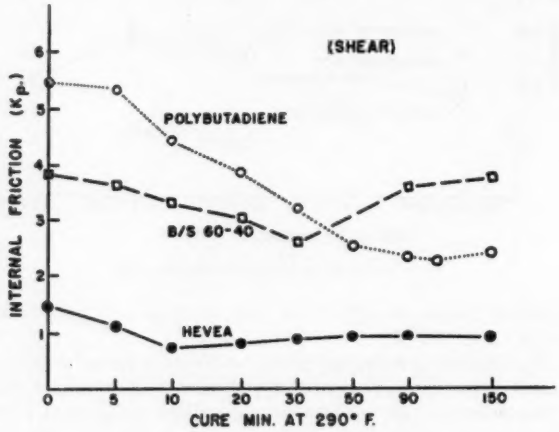

FIG. 15.—Internal friction vs. cure.

into the vulcanization reaction, is evidently responsible for this difference in behavior on vulcanization. It is reasonable that it should affect markedly the type of cross-linked structure which occurs on vulcanization. Possibly other compound formulations would develop better resilience values in high styrene copolymer vulcanizates.

Figures 18 and 19 present the results of measurements on a series of buta-

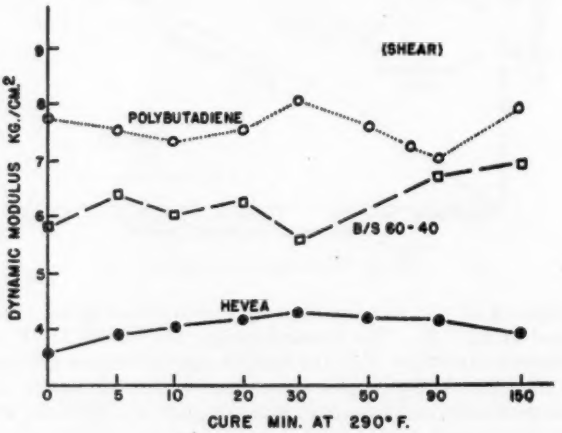

FIG. 16.—Modulus vs. cure.

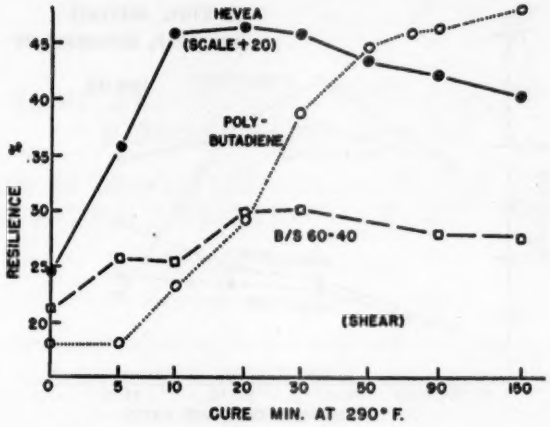

FIG. 17.—Resilience vs. cure.

diene-ethyl acrylate and butadiene-butyl methacrylate copolymers for both raw polymers and gum stocks cured with compound formula A. The effect of increasing the charging ratio of ester for the raw polymers is similar to the results previously given for styrene copolymers. The cured polymers in this series have the highest resilience for a 70/30 butadiene-ester charging ratio.

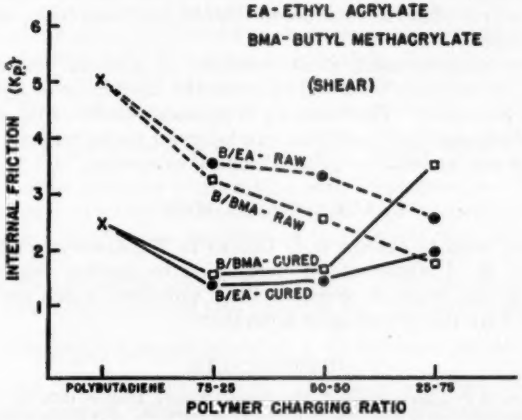

FIG. 18.—Internal friction vs. charging ratio.

SUMMARY

Theoretical considerations made it probable that the usefulness of measurements of vibrational properties of vulcanizates to evaluate rubberlike qualities and heat generation under flexing might be extended to raw polymers if a suitable technique of measurement could be found. Such a technique was developed and correlations between dynamic properties of raw polymers and vulcanizates were studied.

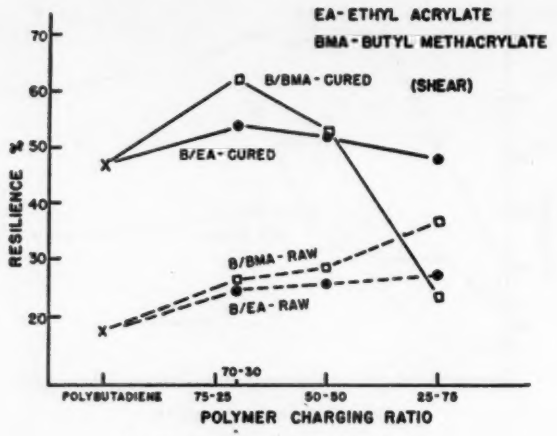

FIG. 19.—Resilience *vs.* charging ratio.

The test conditions, using low amplitude shear vibrations at 60 cycles per second, were such that effects due to plastic flow in raw polymers were suppressed and values of dynamic modulus and resilience were independent of plasticity. The data obtained showed a definite correlation between the dynamic properties of a series of raw polymers and those of vulcanized gum and tread stocks prepared from them. The effect of cure was measured throughout a range from the raw state to overcure for Hevea, polybutadiene, and butadiene-styrene copolymers.

The ease of measurement, small quantity of material required, and the nature of the correlations observed indicate the usefulness of dynamic evaluations for raw polymers. Furthermore, it appears possible, with suitable background, to anticipate fairly well from raw polymer measurements the dynamic properties that can be achieved in a vulcanized compound.

ACKNOWLEDGMENT

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SOME PROPERTIES OF VULCANIZED RUBBER UNDER STRAIN

DEGREE OF CRYSTALLIZATION AS CALCULATED FROM TEMPERATURE COEFFICIENT OF ELASTIC TENSION *

B. B. S. T. BOONSTRA

RUBBER-STICHTING, DELFT, HOLLAND

The change with temperature in the elastic force, f, of stretched vulcanized rubber has attracted attention because of its positive value as distinct from most other elastic materials, *e.g.*, steel springs. This has led to the development of the now generally accepted Mark-Guth-Kuhn theory of kinetic-statistical causes of the rubberlike elasticity. This theory shows the elasticity of rubber to be principally different from that of a steel spring and the elastic force to be very nearly related to the reaction force experienced when a gas is compressed under a piston in a cylinder.

Wiegand and Snyder[1] treated the rubber pendulum, an application of the so-called Gough-Joule effect, thermodynamically and determined the temperature coefficient of the elastic tension at elongations up to 700 per cent. At these high elongations they found a negative value for the coefficient, a fact which has not been confirmed by later authors. These experiments of Wiegand and Snyder are, however, obscured by relaxation of stress. The rate of relaxation increases rapidly with increasing temperature, thus causing considerably lower tension. It is hardly possible to speak of a temperature coefficient in their case, as the change in tension is far from reversible. Meyer and Ferri[2] measured $\left(\frac{df}{dT}\right)_L$ accurately at small elongations and found this term to be proportional to the absolute temperature only if corrected for thermal expansion. Meyer and van der Wijk[3] mention that this correction should not be applied in such a simple way, agreeing in this respect with Elliott and Lippmann[4].

Accurate measurements with natural rubber and GR-S pure-gum vulcanizates at various elongations are also reported by Roth and Wood[5].

In this laboratory, measurements of $\left(\frac{df}{dT}\right)_L$ were carried out by Wildschut[6], who first correlated the drop in elastic force on crystallization with the degree of crystallization. Later a more accurate treatment of the correlation, between degree of crystallinity and the resulting decrease in elastic tension was given by Flory[7].

Similar experiments, described in the present paper, were carried out with two well defined pure-gum vulcanizates at different elongations. The crystallinity was estimated by determination of the heat of crystallization and change in internal energy.

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TEMPERATURE COEFFICIENT OF ELASTIC TENSION AT VARIOUS ELONGATIONS

Experimental procedure.—The mixes were vulcanized in a steam-heated press into sheets about 0.5 mm. thick. From these sheets 33.4 × 36.7 mm. rings were punched, and these were stretched over pulleys about 3 mm. in diameter. Rings proved to be preferable to dumbbell samples, as the latter need constant adjustment, owing to different contraction of the narrow and broader part of the dumbbell when the temperature is increased. As with the rings described there is still about 10 per cent difference between outer and inner diameter, another type of sample was tried—a ring 25 and 26.2 mm. thick and about 3.5 mm. broad. Although here the small difference between inner and outer diameter warrants a more homogeneous elongation, molding difficulties reduced the accuracy of the results with these samples to about the same amount as with the flat rings.

TABLE I

TEST MIXTURES

	S	T
Smoked sheet rubber	100	—
First latex crepe	—	100
Zinc oxide	5	5
Captax	0.8	—
Diphenylguanidine	0.5	—
Aldol α-naphthylamine	1	—
Tuads	—	3
Stearic acid	1	1
Sulfur	1.75	—
Vulcanization at 142° C in press, min.	20	30
Tensile strength, kg./sq. cm.	320	265
Elongation at rupture, %	680	755
Load at 300% elongation, kg./sq. cm.	22	10.5
Hardness (Shore A)	38	29
Elasticity (Shore B)	97	90
Permanent set after 24 hours, 200% elongation measured 24 hours after release, %	1	0
Specific weight	0.97	0.96

The apparatus consisted of a jacketed vertical glass tube in which the sample was fastened to the bottom and the other end was suspended from the beam of a laboratory balance with a sensitivity of about 0.05 gram.

The rings were put in the apparatus at the highest temperature of the range of the measurement, stretched to the desired elongation, and kept there until further stress relaxation during measurements was negligible. For elongations up to 300 per cent the highest temperature was 70° C and the relaxation period 0.5 or 1 hour. After this period the temperature was lowered 0.5° C per minute to the lowest temperature (usually −40° C), and after that, increased again until the original value had been reached.

The experiment was considered satisfactory when the tension after this cycle amounted to practically the value shown at the start. However, at elongations of 300 per cent and higher, the tensions of the return (increasing temperature) lay for an important temperature region at much lower values than for decreasing temperatures. The tension-temperature curves at decreasing temperature were used for the calculations, on the argument that they must be nearer to the true equilibrium than the ascending branch of the curve. The latter contain less amorphous (mobile) rubber and, therefore, are less

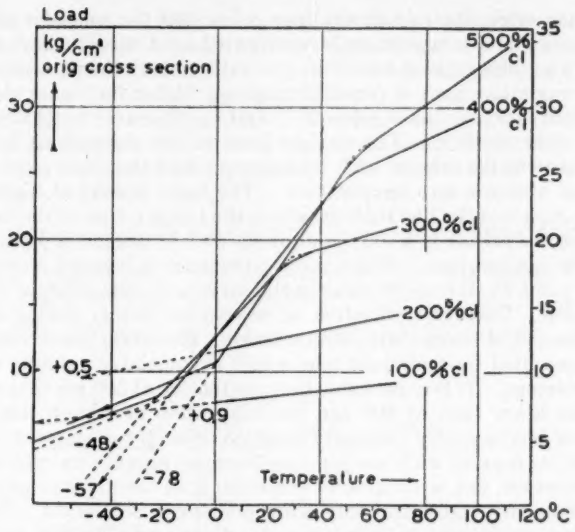

FIG. 1.—Tension-temperature relationship for mix S.

capable of reaching equilibrium (between stress and orientation or crystallization) than the more amorphous rubber which is present before the temperature was lowered.

The measurements were repeated three or more times, and the average of the slopes and tension values is plotted in Figures 1 and 2. No corrections for thermal expansion were applied.

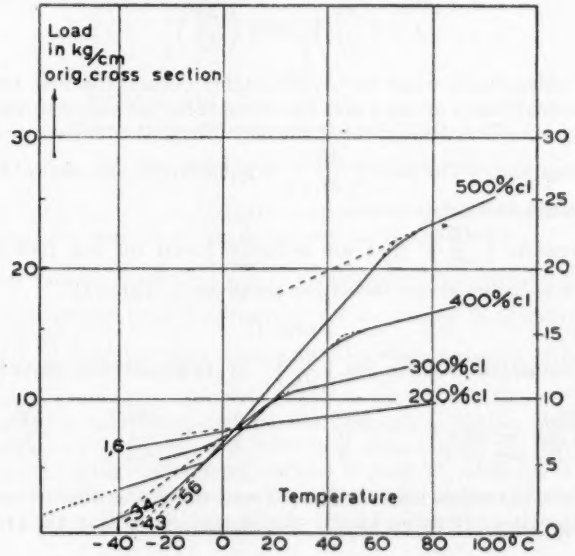

FIG. 2.—Tension-temperature relationship for mix T.

Discussion of results.—At elongations below 300 per cent the relationship between tension and temperature is represented by a straight line; at 300 per cent and higher elongations, however, two rather sharp bends become visible. One, occurring above zero, is found increasingly higher for higher elongations; the other, less sharp, is found below 0° C and has the same trend but is less reproducible than the first. The straight lines at low elongations indicate the proportionality of the tension with temperature, and therefore must yield zero intercepts at absolute zero temperature. The same is valid at higher elongations for that part of the line that lies above the temperature of the first discontinuity; here the rubber is wholly amorphous and its tension is proportional to the absolute temperature. When the temperature is lowered, crystallization sets in at a point *Ti* (the upper break in the curve), the temperature of incipient crystallization. Then crystallization increases with further cooling and causes a steeper descent of tension with temperature. However, the relationship can still be represented by a straight line, which extrapolated exhibits a strongly negative intercept. It is remarkable that the tension at 500 per cent elongation may become lower than at 400 per cent elongation at certain temperatures. At still lower temperatures a second transition point is encountered; below this the decrease of tension with temperature resumes roughly its original course. This can, however, not be accurately determined, as the measurements are less reproducible in this region and only a few points can be plotted. The second discontinuity would indicate that below this point crystallization no longer increases or increases only at a much reduced speed. These low-temperature discontinuities lie well above the second-order transition point of natural rubber (−72° C) and even definitely above the brittle point (−58° C).

ENERGY EFFECTS ON STRETCHING

If an approximate equilibrium is assumed at the various temperatures, the tension may be represented by:

$$f = \left(\frac{dE}{dL}\right)_T + T\left(\frac{df}{dT}\right)_L$$

At low elongations, when no crystallization occurs, the first term on the right is practically zero or has a small positive value; at higher elongations this is valid only at sufficiently high temperatures (above the temperature of incipient crystallization). The term $\left(\frac{dE}{dL}\right)_T$ is equal to the intercept of the tension axis at absolute zero temperature.

The values for $\left(\frac{dE}{dL}\right)_T$ that are actually found for the plot above the temperature of incipient crystallization are given in Table II.

TABLE II

EXPERIMENTAL VALUES FOR $\left(\frac{dE}{dL}\right)_T$ AT TEMPERATURES ABOVE *Ti*

Elongation (%)	300	360	400	500	550
S compound (kg./sq. cm.)	0	−1	−4	−12	—
T compound (kg./sq. cm.)	0	—	−2	−7	−15

These data show that only for 300 per cent elongation the rubber above *Ti* behaves approximately as an ideally elastic material within the errors of the

measurements (about ±1 kg. per sq. cm.). If we are really determining equilibrium values, this means that above 300 per cent elongation and at temperatures above *Ti* there are still effects which result in decrease of energy on stretching. Such effects have been called procrystallization, as probably some crystallites are formed during the cooling in this temperature region.

At *Ti* crystallization sets in on a larger scale and consequently the tension decreases more rapidly with temperature. This has been shown clearly before by several investigators.

It is interesting to mark the value of $\left(\frac{dE}{dL}\right)_T$ in the temperature region of increasing crystallization. Here the intercept is strongly negative because of the heat of crystallization which develops.

In Figure 3 the value of $\left(\frac{dE}{dL}\right)_T$ is computed for various elongations.

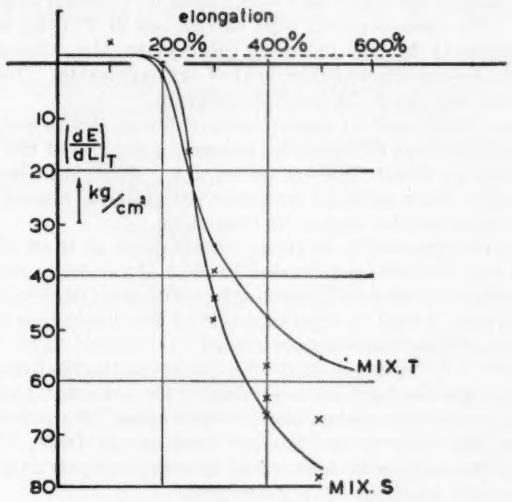

FIG. 3.—Internal energy as a function of elongation.

This curve holds not for one definite temperature but for the whole range of temperatures, the breadth of which depends on the elongation.

The curves in Figure 3 for $\left(\frac{dE}{dL}\right)_T$ *vs.* elongation may be integrated up to 300, 400, and 500 per cent, respectively. This integral is proportional to the value of $\int\left(\frac{dE}{dL}\right) dL$ for these cases, *i.e.*, the actual change in internal energy on stretching.

This energy calculated from the surface area, say to 500 per cent elongation, is the latent heat of crystallization developed when the sample is stretched 500 per cent, provided that other energy effects of positive value due to increase in interatomic distances or distortion of valence angles remain small. At about 20° C the values for S and T compounds are those listed in Table III.

TABLE III

CRYSTALLIZATION ENERGY DEVELOPED ON STRETCHING TO VARIOUS ELONGATIONS

(Values in joules per cc.)

Elongation (%)	300	400	500
S compound	1.6	7.5	14.0
T compound	1.6	5.8	10.8

If the heat of crystallization of pure rubber is known, the degree of crystallization at these three elongations can be estimated in this way.

LATENT HEAT OF CRYSTALLIZATION AND DEGREE OF CRYSTALLIZATION AT VARIOUS ELONGATIONS

In 1929, van Rossem and Lotichius[8] determined the heat of crystallization of frozen first latex sheets which had been stored for between 10 and 14 years in a cool cellar. The measurements were carried out at 0° C by swelling frozen and thawed sheets in toluene in an ice calorimeter; the difference in heat of swelling of the two specimens is the heat of crystallization. The value found by these authors was about 5.0 calories per gram.

This has been confirmed by experiments of Wood, Bekkedahl, and Gibson[9], who determined the heat of fusion by measuring the rise of the melting point through pressures of about 1200 kg. per sq. cm. Applying Clapeyron's equation, they found a value of about 4 calories per gram for a stark rubber which they considered not crystallized to its final value.

The degree of crystallinity of frozen sheets, such as those studied by van Rossem and Lotichius, can be estimated to 30 to 35 per cent according to x-ray analysis by Arlman and Goppel[10], which agrees with their density measurements. This would indicate a heat of crystallization of the crystallites of 14.5 to 16.8 calories per gram (60 to 70 joules per gram).

Experimental.—As no accurate measurements of the heat of crystallization of rubber with a known degree of crystallinity are available, the author determined this property with smoked sheet rubber about 35 years old, which had been stored in the cellar of the Rubber Institute at Delft. The degree of crystallinity of this sample as determined by x-ray analysis and density measurements amounted to about 38 ± 2 per cent.

The calorimeter was of the twin Dewar flask type, and the compensation heating method was used in most of the experiments.

The temperature indicator was a mirror galvanometer sensitive to about 10^{-8} ampere, in combination with a tenfold copper-constantan thermocouple series.

About 1 gram of frozen rubber was swollen in 25 cc. of toluene and the decrease in temperature was compensated by electrical heating. The experiments were repeated with amorphous rubber, obtained by heating the frozen sheets to about 70° C for about 15 minutes. The thermostat containing the Dewar flasks was kept constant at 0° C with ice water.

The heat of swelling of frozen rubber (sheets 52 T) was determined as the average of ten measurements.

Crystallized rubber, average	34.7 ± 3.0 joules
Thawed rubber, average	4.9 ± 1.2 joules
Crystallization	30 ± 4.2 joules

Measurements at 11° C carried out at the University of Groningen with the same rubber gave lower results.

Swelling frozen sheets	23.0 ± 2.0 joules
Swelling thawed sheets	0.95 ± 0.08 joule
Crystallization energy	22 ± 2 joules

Taking the average heat of crystallization 25 joules per gram for the 38 per cent crystallized sheets, the latent heat of crystallization for the crystallites is computed as 66 joules per gram. This may be compared with the heat of melting of isoprene at 126° C, which amounts to 70.9 joules per gram[11].

Taking into account the specific weight of the S and T vulcanizates and their crude rubber contents, total crystallization would develop 58 joules per cc. of vulcanizate.

With this figure as a base, we can evaluate the energy effects in stretching mentioned in Table III.

In Table IV the degree of crystallinity calculated from Table III is compared with the figure determined by direct x-ray analysis taken from the investigation of these compounds by Arlman and Goppel[10].

TABLE IV

DEGREE OF CRYSTALLINITY COMPUTED BY ENERGY MEASUREMENTS AND DETERMINED BY DIRECT X-RAY ANALYSIS

Elongation, %	Method	S Compound, %	T Compound, %
300	Energy	2.8	2.8
	X-ray	4	5
400	Energy	13	10
	X-ray	15	10.5
500	Energy	24	19
	X-ray	30	19–22

It is obvious from Table IV that there is fair agreement between the energy-computed crystallization figures and those measured by direct x-ray analysis, though the energy tends to yield somewhat lower values. As neither method gives very accurate figures, a better agreement is not to be expected.

CONCLUSION

The degree of crystallization of stretched vulcanized pure-gum compounds can be determined by calculating the differential and integral energy effects on stretching from the elastic tension *vs.* temperature measurements, on the assumption that the plots represent equilibrium tension values. The percentage of crystallinity figures calculated in this way at various elongations agrees fairly well with figures obtained by direct x-ray measurements.

SUMMARY

To elucidate the crystallization phenomenon in natural rubber and to investigate the applicability of thermodynamic calculation to measurements of the elastic tension as a function of temperature, it seemed necessary to check whether crystallization determined by x-ray analysis (and combined with density) lined up reasonably with the percentage of crystallization computed from the energy change found by applying thermodynamics to stretched vul-

canized rubber) on stretching. Calorimetric measurements were desirable, as no accurate figures are available for the heat of crystallization of rubber crystallites.

The heat of melting of rubber crystallites was determined to about 66 joules per gram, which is of the same order as that of isoprene. The spreading in the results was large; the determination is based on the degree of crystallization found by x-ray analysis of raw rubber. The heat of crystallization on stretching, found by thermodynamic evaluation of the elastic tension and its temperature coefficient, is combined with the value of 66 joules for the heat of melting of the pure rubber crystallites. The degree of crystallization calculated in this way agrees reasonably well with the direct x-ray measurements of Goppel and Arlman.

Crystallization as determined by x-ray analysis and that responsible for the energy change on stretching are much the same. This also means that thermodynamic evaluation of the change of stress with temperature is justified if sufficient relaxation of stress has taken place.

ACKNOWLEDGMENT

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THE EFFECT OF SULFUR ON THE OXIDATION OF SODIUM-BUTADIENE RUBBERS *

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In the vulcanization of rubber and in the service performance of vulcanized rubber products, oxygen and free sulfur are always present. Consequently it is important to know the effect of sulfur on the oxidation of rubber. The present work is devoted to an investigation of the oxidation of a sodium-butadiene polymer in the presence of sulfur[1].

Dogadkin and his associates[2] established the fact that oxygen has an influence on the nature of the structural changes of rubber during vulcanization.

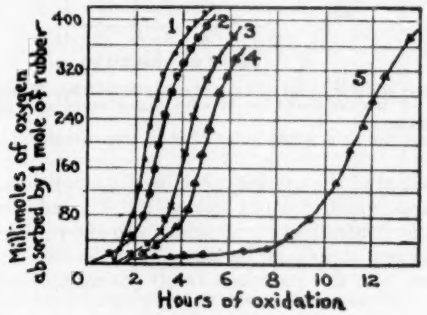

Fig. 1.—Curves of the kinetics of the oxidation of rubber containing various percentages of sulfur.

1.—No sulfur.
2.—0.09 per cent sulfur.
3.—0.18 per cent sulfur.
4.—0.25 per cent sulfur.
5.—0.61 per cent sulfur.

The present authors have shown that any sulfur which is chemically combined with rubber does not appreciably affect the kinetics of its oxidation, and that free sulfur, in solution in rubber, interferes with autocatalytic oxidation. The higher the concentration of sulfur, the greater is this interference (see Figure 1). Introduction of sulfur into rubber during autocatalysis does not prevent the autocatalytic process, but hinders it noticeably (see Figure 2). The introduction of a secondary aromatic amine has been observed to arrest the process altogether[3]. This behavior of sulfur can be explained by its ability to react with intermediate oxidation products, since the rate of combination of sulfur is practically constant[4] (see Figure 3).

In the form of volatile oxidation products of rubber, both in the absence as well as in the presence of sulfur, formic acid and formaldehyde are formed;

* Translated for Rubber Chemistry and Technology by Alan Davis from *Reports of the Academy of Sciences, USSR*, Vol. 75, No. 2, pages 223–226 (1950).

however, in the presence of sulfur, a smaller total quantity of volatile substances is formed; nevertheless, the ratio of formic acid to formaldehyde remains constant.

The equilibrium concentration of peroxides in the presence of sulfur is notably lower than in its absence; it follows that the balanced concentration of free radicals is also lower in the presence of sulfur.

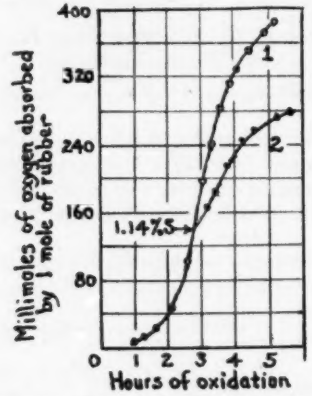

FIG. 2.—Influence of sulfur on the rate of autocatalytic oxidation of rubber when sulfur is added during the intensive stage of oxidation.

1.—No sulfur.
2.—1.14 per cent sulfur added during 2.7 hours after initiation of oxidation.

The rubber studied in the present work, under conditions of a high vacuum and at temperatures which did not exceed 90° C, underwent practically no structure formation. Introduction of sulfur into the rubber in an atmosphere of pure nitrogen caused structure formation and the loss of 16 per cent of the initial unsaturation. In this process a small quantity of sulfur was bound. A

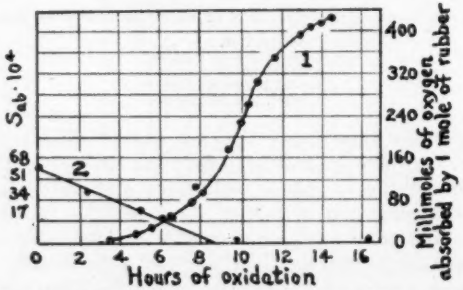

FIG. 3.—Kinetics of consumption of sulfur during the oxidation of rubber. At the initial moment of oxidation the concentration of sulfur was 0.3 per cent (0.084 mole per liter).

similar experiment at 143° C gave the same small decrease of free sulfur. It may be assumed that this consumption of sulfur is related to traces of oxygen present in the system.

All this leads to the conclusion that the reactions of rubber with oxygen and with sulfur are an interrelated process. The oxygen starts a chain process,

which results in the formation of free radicals, which react with the oxygen, sulfur, and original rubber at the double bonds of the latter, or which become inactive as a result of regrouping or of some other process. Oxidation leads to rupture of the molecular chains, and polymerization causes structure formation[5].

The activation energy of the initiation of the union of oxygen with rubber at the double bonds of the main chains was 22.5 kcalories per mole[6].

The activation energy of vulcanization was 27 kcalories per mole. This indicates that the rate of reaction of rubber with oxygen is much faster than that with sulfur.

The basic qualitative difference between the action of oxygen and that of sulfur is that sulfur does not form any unstable intermediate products of the type of peroxides. Polysulfides do not start a chain reaction.

The length of the oxidizing chains[7] is proportional to the probability of formation of a chain; this depends on the concentration of double bonds in the rubber (C) and, in turn, is proportional to the probability of rupture β. By this is meant only rupture with the inhibitor, since in films of rubber the probability of regrouping is slight.

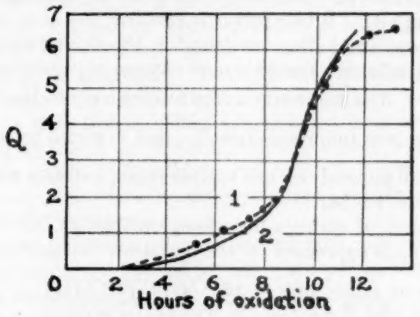

FIG. 4.—Oxidation curves of rubber containing no sulfur.
1.—Experimental.
2.—Theoretical.
Q is the number of moles of oxygen absorbed per liter of rubber.

The probability of rupture for the inhibitor β_i is proportional to the concentration of the latter; that is, $K_i = \sigma_i[i]$. If this concentration is 1 gram-mole per liter of rubber, $K = \sigma_i$, that is, it is equal to the molecular constant of rupture for the given inhibitor. The role of the latter in our experiment was played by the oxygen and sulfur.

The rupture constants for oxygen and for sulfur (σ_{O_2} and σ_S) are expressed by the equations:

$$\sigma_{O_2} = \frac{C}{\gamma_1[O_2]} \qquad \sigma_S = \frac{C - \sigma_{O_2}[O_2]\gamma_2}{\gamma[S]} \tag{1}$$

where γ_1 is the length of an oxidizing chain in the absence of sulfur, and γ_2 the length in the presence of sulfur.

The lengths of the chains can be determined during the static period of oxidation (in the segments of maximum rates). At this stage of oxidation, the rates of formation and decomposition of the peroxides are equal, and inasmuch as the rate of consumption of oxygen in the chain reaction is greater than the

rate of decomposition of the peroxides, the relation of these quantities gives the length of the chain.

During the oxidation of sodium-butadiene rubber, when 90° $\gamma_1 = 3.1$, if 0.3 per cent sulfur is introduced into the rubber, γ_2 (90°) = 1.8. From these values, it follows that $\sigma_{O_2} \cong 1000$ and $\sigma_S \cong 62$, that is, the probability of rupture for sulfur is 16 times smaller than the probability of rupture for oxygen, provided the concentration of both elements is equal. If account is taken of the fact that, with the introduction of 3 per cent of sulfur, the initial concentration of the latter is 23 times greater than the concentration of oxygen dissolved in the rubber, then the probability of rupture for both substances in the initial stages of the reaction is approximately the same[8].

It has been shown that the rate of autocatalytic oxidation of rubber ($w_{\bar{O}_2}$) is expressed satisfactorily by the relation[3]:

$$w_{\bar{O}_2} = K_2[C][P] \tag{2}$$

where P is the concentration of peroxides. K_2 includes the constant of the rate of reaction of the radicals with oxygen ($K_{\bar{O}_2}$), the ratio of the equilibrium concentrations of peroxides and radicals, k, and, in the denominator, the rupture constant for oxygen σ_{O_2}. When sulfur is present, the sum of the probabilities of rupture for oxygen and sulfur are found in the denominator.

Since the total rate of absorption of oxygen w_Q^+ includes the rate of the secondary reactions, it is necessary to introduce a correcting factor into Equation 2. This factor was found empirically, and is equal to $\frac{1}{1 - n[Q]^{-\frac{1}{2}}}$, where n is a constant which depends on the temperature, and Q is the concentration of oxygen bound by the rubber.

For the oxidation of sodium-butadiene rubber at 90° C, the kinetics of absorption of oxygen is expressed by the equation (without sulfur):

$$w_Q^+ = \frac{8.68 \times 10^{-5} \times [C][P][O_2]}{(4.3 + 16[S])(1 - 0.2[Q]^{-\frac{1}{2}})} \tag{3}$$

Figure 4 shows the experimental curve of absorption of oxygen during the oxidation of rubber containing sulfur, and the corresponding curve constructed according to Equation 3.

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RELATION OF PEROXIDE DECOMPOSITION TO RUBBER DEGRADATION *

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A controlled amount of oxidative degradation of natural rubber is required for mastication and for preparation of highly softened, "depolymerized" rubbers[1]. The importance of oxygen in mastication has recently been stressed by Blow and Wood[2], who have shown that little breakdown occurs in absence of oxygen even when chemical plasticizers such as mercaptobenzothiazole are used. It is now generally agreed that the first recognizable product of autoxidation of rubber and other olefins is a peroxide, and it appears probable that oxidative scission occurs largely if not entirely as a result of peroxide decomposition; possible mechanisms of decomposition of hydroperoxides have been discussed—for example, by Farmer[3] and by George and Walsh[4]. In a survey of oxidative degradation of polymers, Tobolsky[5] concludes that at low temperatures the George and Walsh mechanism is probably the most important; the general postulate is that fission of the O—O bond to give an RO· radical is normally followed by fission of the weakest adjacent C—C bond to yield an aldehyde or ketone and a hydrocarbon radical. As Farmer has emphasized, only a small fraction of the decomposing peroxide actually causes scission, but this fraction is of vital importance.

In protecting rubber from oxidative degradation, most of the normal antioxidants act by reducing the rate of oxygen absorption, probably by acting as H-atom donors to the free radicals involved in the chain propagation process of peroxide formation, as indicatedby Boll and and ten Have for phenolic inhibitors[6]. Le Bras and his co-workers[7], however, stated that another mode of protective action exists and that certain compounds, such as mercaptobenzimidazole, can retard the deterioration of physical properties without appreciably altering the rate of oxygen intake. It was suggested that these substances act by deactivating the peroxides formed.

It appeared, therefore, that the reactions of peroxides with mercaptobenzimidazole (MBI) would be worth some consideration, and that a comparison with the reactions of mercaptobenzothiazole (MBT) and also with simpler compounds such as thiourea and thioamides would also be of interest. Both MBI and MBT yield the corresponding disulfides on mild oxidation, whereas hydrogen peroxide in excess can bring about further oxidation; in alkaline solution, 2-hydroxybenzimidazole and 2-hydroxybenzothiazole are formed, and in acid solution, benzimidazole and benzothiazole are formed[8] from MBI and MBT, respectively. The reactions between thiourea and peroxides have been more thoroughly investigated, particularly by Böeseken[9]. In acid solution, thiourea is oxidized to the cation of formamidine disulfide; the free disulfide is unstable and decomposes to give thiourea, sulfur, and cyanamide.

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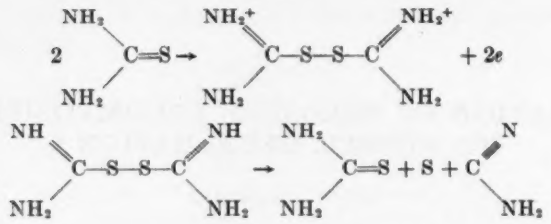
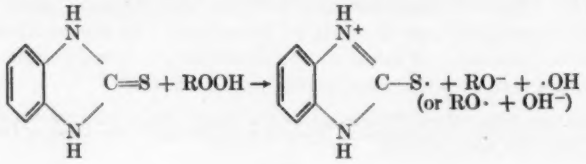


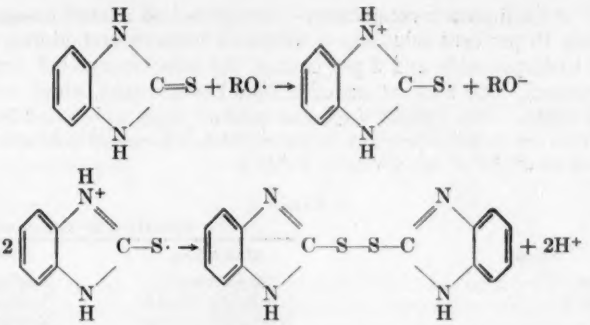
In neutral solution, the calculated amount of peroxide (hydrogen peroxide or peracetic acid) yields formamidinesulfinic acid, but additional peroxide gives the sulfonic acid. The latter is less stable than the sulfinic acid. In alkaline solution, hydrogen peroxide gives urea as a final product, derived from the hydrolysis of the sulfonic acid. Priesler and Berger[10] found that the thiourea-formamidine disulfide system was reversible and obtained accurate oxidation-reduction potentials for thiourea and many of its derivatives. These were, of course, restricted to the pH range over which the disulfides were stable.

REACTIONS OF PEROXIDES WITH MBI AND RELATED COMPOUNDS

The published work does not, however, establish a detailed mechanism for reactions of these sulfur compounds with peroxides. Preliminary experiments on the reaction between MBI and *tert*-butyl hydroperoxide showed a number of interesting features: the reaction was exothermic, and oxygen was evolved under certain conditions. For example, a solution of 1 gram of *tert*-butyl hydroperoxide and 0.1 gram of MBI in 10 cc. of *tert*-butyl alcohol gave a rapid stream of bubbles of oxygen over a period of 2 hours at 70° C. Replacing the solvent by a 1:1 mixture of *tert*-butyl alcohol and benzene had little effect, but when either isopropyl alcohol or cyclohexene was used in place of benzene, no oxygen was evolved. It was also noted that some acetaldehyde was formed when ethyl alcohol was used as solvent.

These observations suggested a similarity to the hydrogen peroxide–ferrous salt reaction[11]. The suppression of oxygen formation with isopropyl alcohol and cyclohexene was particularly significant, since these solvents are readily attacked by ·OH and alkoxy radicals. Further evidence that a free radical mechanism was involved in these peroxide reactions was given by thiourea. The addition of hydrogen peroxide and a trace of thiourea to hydrochloric acid solutions of a number of aromatic amines gave in all cases the same color reactions as those obtained with the hydrogen peroxide–ferrous salt test for these compounds. It seemed, therefore, that MBI, thiourea, and probably other related compounds could undergo a one-electron transfer to hydrogen peroxide and alkyl hydroperoxides and could, therefore, initiate attack on other compounds in the same way as other reduction activators. The initial reaction between MBI and a hydroperoxide would thus have to be formulated:

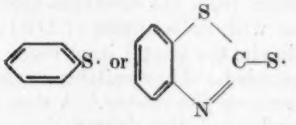




The thioketone structure for MBI has been used here because the infrared spectrum shows that this and not the thiol structure is the correct one[12]; compare MBT which also has the thione structure[13].

A solution of cyclohexene hydroperoxide (0.033 *M*) in benzene in the presence of 0.016 mole per liter of MBI showed complete decomposition of the peroxide in 100 hours at 25° C, whereas a similar solution in cyclohexene gave an initially faster rate of decomposition. This, however, ceased when 0.016 mole of peroxide had decomposed. It has generally been found that the amount of peroxide decomposed was less when a readily attacked solvent was present. Incidentally, there was no detectable decomposition of either cyclohexene or *tert*-butyl hydroperoxides within 100 hours at 30° C in the presence of phenyl-β-napththylamine, as a typical antioxidant of the normal type; this is in striking contrast to the behavior of amines with benzoyl peroxide[14].

During the early stages of the peroxide oxidation of MBI in fairly concentrated solutions, a deep yellow color develops, and then fades as the disulfide begins to separate. A similar color is also seen in the oxidation of thiophenol to diphenyl disulfide. Solutions of both diphenyl disulfide and MBI disulfide show thermochromasy, developing reversibly a yellow color on heating. In diphenyl disulfide[15] and in the similar case of MBTS[16] it has been established that the color is due to thermal dissociation into the radicals:



and this is almost certainly the case for MBI also. It is probable, therefore, that the color during oxidation is due to the presence of the same free radicals; in this event, it would appear that the dimerization of the radicals is rather slow compared with the rate of formation. In the case of MBI, the yellow color of both the oxidizing solution and the hot disulfide solution are intensified by acid.

PEROXIDE ATTACK ON RUBBER IN PRESENCE OF MBI AND RELATED COMPOUNDS

The evidence presented suggested that the presence of MBI and a peroxide in rubber would lead to attack on the rubber and probably result in degradation. In fact, when MBI and an excess of either *tert*-butyl or cumene hydroperoxide was added to a benzene solution of natural rubber, a rapid decrease in viscosity

followed. A preliminary comparison of a number of related compounds was made, using 10 per cent solutions of rubber in benzene and adding 5 per cent *tert*-butyl hydroperoxide and 2 per cent of the other compound (both on the rubber content). Air was not excluded from the solutions, which were kept in stoppered tubes. The rubber used was smoked sheet which had been lightly milled before use to aid dispersion in the solvent. Viscosities determined after 4 and 21 days at 20° C are given in Table I.

TABLE I

Solution	Viscosity at 20° C (poises)	
	After 4 days	After 21 days
No addition	90 (approx.)	Negligible change
Peroxide only	Negligible change	Negligible change
MBI only	Negligible change	Negligible change
Peroxide plus		
tert-Butyl thiol Dodecyl thiol MBI disulfide	Negligible change	Negligible change
Sodium diethyldithiocarbamate	18	10.9
Thiophenol (benzenethiol)	10.8	5.8
MBT	7.25	3.7
Thiourea	0.95	0.81
Vulcamel (α-naphthalenethiol)	1.09	0.80
Thioacetamide	1.28	0.56
MBI	0.50	0.29
Ethylenethiourea	0.18	—

Most of the compounds which are effective contain thiocarbonyl groups and all except thioacetamide are readily oxidized to disulfides. (Thioacetamide gave no indication of disulfide formation in potentiometric titrations with iodine; in acid solution sulfur was precipitated, and the end point corresponded with oxidation to acetamide + sulfur.) Aromatic thiols are effective in promoting degradation, and aliphatic thiols are inactive (at least under the conditions used here). Thiouracil and 2-mercaptothiazole are also moderately effective, but 2-ethyl-mercaptobenzimidazole is quite inactive.

To decide whether oxygen was required for the degradation, cumene hydroperoxide was used instead of *tert*-butyl hydroperoxide, since there was less danger of oxygen evolution from the peroxide-MBI reaction. Solutions of natural rubber in benzene with the addition of MBI and peroxide were sealed one in nitrogen and one in air: the sample in nitrogen gelled within 2 days, and the air specimen was degraded. The available oxygen in the latter case was approximately 0.25 per cent on the rubber. A slow stream of oxygen passed through the solution accelerated the degradation. Diffuse daylight had a slight accelerating effect on the degradation during the early stages, but after 2 or 3 days the differences in solution viscosities of light and dark samples were negligible. A more detailed comparison of the reagents is still in progress, but it is already apparent that the relative efficiencies and to some extent the order of the activities depends on the conditions. With lower concentrations of the reagents, the relative viscosity differences of the solutions are greater; ethylenethiourea is particularly outstanding. With the most active reagents, the degradation occurred mainly in the first few hours. In this comparison, 5 per cent benzene solutions were used, with 0.015 mole of *tert*-butyl hydroperoxide (used in the form of the commercial product containing some di-*tert*-butyl peroxide, assumed to be inert) and 0.004 mole of the second substance per 100 grams of rubber. The sample vessels were stoppered to prevent evapora-

tion, but were filled in air. The products recovered from the lower viscosity solutions were viscous liquids (Table II).

TABLE II

Compound added (in addition to peroxide)	Viscosity at 20° C (poises)		
	2 days	12 days	36 days
Ethylenethiourea	0.16	0.12	0.10
MBI	25.3	8.41	0.55
Thiourea	29.0	2.42	0.30
Zinc diethyldithiocarbamate	—	15.2	4.93
MBT	—	—	22.1

Addition to Hevea latex of peroxide and MBI also results in degradation. The general method used was to add peroxide followed by MBI (or one of the other compounds under consideration) to the latex, allowing to stand for varying periods, and then preparing rubber films by drying thin layers of latex. In the early stages, changes in these films were followed by measuring extension-time curves under a constant tensile stress. (Correction for changes in cross-section was made by applying the load through a cam of the appropriate contour.) Small variations in thickness in the dumbbell test pieces occurred, leading to differences in applied stress, but it was found that a sufficiently accurate correction to a standard stress could be made by assuming a linear relation between stress and strain over the small range encountered. The stress was approximately 4×10^6 dynes per square cm. Some films became too soft and tacky to be examined physically in this way.

A comparison of the influence of varying concentrations of MBI and peroxide was made on ammonia-preserved 60 per cent centrifuged latex, using the following concentrations of MBI and *tert*-butyl hydroperoxide: 0.1, 0.3, 1.0, 3.0 per cent on the latex. Differences in films prepared after a few days; standing were rather small, but with increasing time some samples showed an increasing extensibility. As the curves were similar in general shape, comparison of the samples could be made adequately by using the percentage of extension after a fixed time of application of the stress, usually 5 minutes.

The extensions of samples stored 7 days as latex and 100 days as rubber films (exposed to air but kept in darkness) are given in Table III.

TABLE III

MBI added (%)	Extensions (after 5-minute stress)(%)				
	Peroxide added (%)				
	0	0.1	0.3	1.0	3.0
0	85	—	—	85	—
0.1	—	112	98	230	160
0.3	—	128	109	275	155
1.0	97	114	122	137	140
3.0	—	114	109	90	97

Neither MBI nor peroxide alone had any marked effect under these conditions, and the optimum softening was reached with 1 per cent peroxide and 0.3 per cent MBI. Where considerable degradation occurred, the major part of the breakdown occured in a comparatively short period, after a long induction period during which the rate of change was small. The more heavily degraded specimens in the series showed this at about 3 to 4 months; these specimens reached a state roughly equal to that of a well masticated rubber and then showed little further change in another 4 months. In these samples, the period

of more rapid degradation was preceded by rather sudden development of a surface stickiness, which later disappeared. The slowness of degradation is in contrast to the behavior in solution, and further work is needed to find an explanation of this difference.

Some of the softer products were insoluble even in aromatic hydrocarbons, suggesting that appreciable cross-linking accompanied the degradation. Addition of varying amounts of solvent (benzene and alcohol-benzene mixtures) was made to latex samples, in the hope that the swollen rubber would show less cross-linking; considerable improvement in both rate and extent of breakdown was obtained even with 5 per cent added solvent. Possibly these additions aid the reaction by affecting the particle surfaces or by influencing diffusion of reactants into the rubber as well as by the swelling effect. It has been possible to prepare a plasticized rubber by allowing the treated latex to stand for a few weeks. Preliminary work on latex of lower pH suggests that improved results would be obtained by using neutral or acid latex.

An investigation of the use of MBI and related compounds as plasticizing agents in mastication of solid rubber is being carried out. Evidence has been obtained that softening can be effected by MBI or thiourea alone, especially at higher temperatures. For example, mastication in a Banbury with 0.5 per cent of MBI gave a slightly softer product than the same amount of MBT. (Times of flow of equal amounts in an extrusion plastometer were 1.07 minutes for a control milled without any addition, 0.55 minute for the MBT treated sample, and 0.50 minute for MBI.) Although the product containing MBI was well plasticized and tacky (in the usual rubber technology sense of self-adhesion), the extreme surface stickiness which characterizes MBT plasticized rubber was completely lacking; this probably indicates a more homogeneous molecular-weight distribution. At lower temperatures, the degradation effect is more pronounced if peroxide is added. The most marked feature is that plasticization may be effected in the region of 100° C, where rubber without additions shows much less softening than at either higher or lower temperatures. An example of plasticization on open rolls is shown in Table IV.

TABLE IV

Milling temp. (° C)	Sample	Milling time (min.)	Extrusion time, (min.)
20	Blank	8	1.19
	MBI + peroxide[a]	8	0.59
50	Blank	8	0.53
	MBI + peroxide[a]	8	0.18
100	Blank	2	4.51
	MBI + peroxide[a]	2	0.79

[a] MBI, 0.25%; *tert*-butyl hydroperoxide, 0.5%.

CONCLUSIONS

Most of this work on rubber degradation has been directed towards the possible industrial applications of the reagents, and it is apparent that a fundamental study under more specialized conditions will be needed to establish the mechanism. At present, the available evidence is sufficient to suggest the following scheme as a working hypothesis:

The initial reaction would be the production of hydroxyl or alkoxy radicals from the added peroxide and the sulfur compound. With excess of the latter,

the radicals would presumably be used mainly in reaction with more of the sulfur compound:

$$R_1OOH + R_2S \rightarrow R_1O + OH^- + R_2S^+$$

$$R_1O + R_2S \rightarrow R_1O^- + R_2S^+$$

$$(R_1O^- \xrightarrow{H^+} R_1OH)$$

Attack by the alkoxy (or OH) radicals on the rubber would be by the normal α-methylene hydrogen abstraction, and this would be followed by peroxidation in the presence of atmospheric oxygen and by cross-linking (or possibly non-oxidative degradation) in the absence of oxygen. The sulfur compound would then react with the rubber peroxides as in the first reaction above, leading to scission reactions of the type indicated by George and Walsh[4]. In a previously peroxidized rubber, addition of "external" peroxide may be unnecessary. When MBI is present in large excess compared with the rubber peroxide, it seems possible that both these reactions would occur, leading to the formation of —CH_2—CH=CMe—CHOH— groups, thus deactivating the rubber hydroperoxide. Such a mechanism would reconcile the apparent contradictions between the work of Le Bras and that described in this paper.

The possibility that radicals or radical ions from the various sulfur compounds can attack rubber directly, either by hydrogen abstraction or double-bond addition, must also be considered. Reactions involving further oxidation of the sulfur compounds are also probable side reactions, for example, the formation of sulfinic and sulfonic acids. Incidentally, formamidinesulfinic acid in solutions made slightly alkaline with ammonia can cause degradation in the presence of peroxide.

Finally, as would be expected, at least some of the thiocarbonyl compounds mentioned in this paper are capable of acting as reduction activators of polymerization. A few preliminary experiments have shown that MBI, thiourea, and ethylenethiourea are capable of initiating the polymerization of styrene, acrylonitrile, and methyl acrylate in the presence of *tert*-butyl or cumene hydroperoxides.

SUMMARY

It appeared that an investigation of the reactions between peroxides and deactivators of rubber degradation, such as mercaptobenzimidazole, would help to explain the action of these sulfur compounds. Le Bras, who proposed the use of these compounds, considered that they function by deactivating the peroxides formed by autoxidation.

It was found that mercaptobenzimidazole and simpler related compounds such as thiourea reacted with alkyl hydroperoxides with the formation of hydroxyl or alkoxy radicals and this led to attack on the solvent or on other molecules present, in a manner resembling the action of ferrous salt-hydrogen peroxide. This suggested that rubber would also be attacked and probably degraded. It was found that mercaptobenzimidazole with excess of peroxide gave rapid degradation of rubber in solution if access of oxygen was permitted. Thiourea, thioacetamide, some dithiocarbonates, and aromatic thiols were also effective, but aliphatic thiols and ethylmercaptobenzimidazole were ineffective. Softened or "depolymerized" rubber was prepared by addition of the reagents to rubber solutions or to latex.

The use of these sulfur compounds in the presence of peroxides provides a means of obtaining a controlled amount of breakdown of rubber, and products

ranging from normal plasticized rubber to a viscous liquid can be prepared. Under different conditions, mercaptobenzimidazole may either promote degradation (as shown in this paper) or retard it (as stated by Le Bras), and a possible explanation for this reversal of behavior is suggested.

ACKNOWLEDGMENT

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RUBBER OXIDATION AND ANTIOXIDANT ACTIONS *

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Many experimental investigations into the oxidation or aging characteristics of rubbers have been carried out during the last 30 years. Some have studied changes in physical properties during artificial aging and have linked these with culcanizate composition and with changes occurring during natural aging. Others have studied the kinetics and mechanisms of the chemical reactions involved. Both approaches have contributed much to the general body of knowledge on this subject.

In more recent years, serious attempts have been made to correlate rate and extent of oxygen absorption with changes in physical properties, and conclusions drawn from this work have proved to be of considerable interest[1].

In most of the work reported, however, oxygen absorption experiments were carried out on one sample of rubber, using a laboratory absorption apparatus, and deterioration of the physical properties of different samples were determined after aging for appropriate periods in an aging oven. Alternatively, direct measurement of the oxygen absorption of a tensile specimen during a given period of aging was made, and the properties of different specimens related. To obtain significant results it has proved desirable to carry out a considerable number of repeat experiments and to subject the data to careful statistical analysis.

In an attempt to overcome some of the difficulties inherent in such an approach, a method was developed whereby simultaneous measurement of oxygen absorption characteristics and the change in elastic properties of a single specimen of rubber during aging can be made under closely controlled conditions. It is believed that direct correlations of this nature can lead not only to a much deeper insight into the mechanism of aging, but also to more practical use of present knowledge of the chemistry and kinetics of polymer aging. The investigation reported here is part of a larger investigation designed to lead ultimately to new means of improving age resistance of natural and synthetic rubbers.

THEORETICAL CONSIDERATIONS

The vulcanization and oxidation reactions of rubber show kinetic characteristics of the type usually associated with chain reactions. These reactions, therefore, may be considered conveniently in three stages:

Initiation—kinetically characterized by a period of accelerating reaction.

Steady state—characterized by constant reaction velocity during which the rates of chain initiation and termination are equal.

A stage in which the termination reaction outstrips chain initiation and reaction velocity decays.

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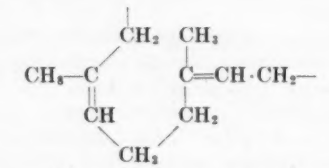
Under the usual conditions of vulcanization involving low sulfur percentages, there is no evidence that requires postulating chain-branching phenomena, which are associated with excessive reaction velocity build-up, although multiplication of reaction chains in this way may occur during the highly exothermic formation of ebonite.

During rubber vulcanization a competitive reaction system exists: the hydrocarbon radical may react either with sulfur or with oxygen, which, unless special precautions are taken, is present, dissolved in the rubber. Also oxidation does not necessarily involve degradation of the polymer chains and it may contribute to the development of desirable physical properties by cross-linkage of polymer chains.

Consider the fragment of the rubber molecule shown in Formula 1. It is evident that the formation of a free radical from such a molecule may occur in at least two ways, involving reactivity of the double bond as illustrated in 1A or of the α-methylenic linkages, 1B.



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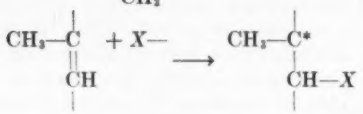
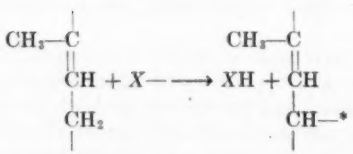


(1A)



(1B)

Although it is well established that hydrocarbons such as 1-methyl-1-cyclohexene give high yields of α-methylenic hydroperoxide, this provides no evidence of the mode of initiations of the reaction, since the subsequent development of the chain may involve many molecules, and the radical type involved in the developing chain is not necessarily that involved in the initiation step.

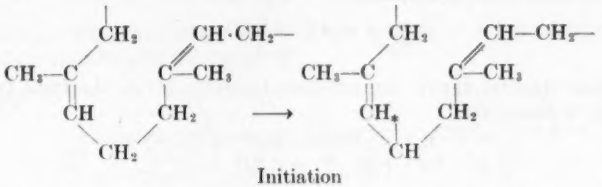
Bolland and Gee[2], from a study of the thermochemistry of oxidative attack on a variety of olefinic substances, found that, for mono-, 1,3-, and 1,4-diolefins, both double bond and α-methylenic attack must be considered as likely, since the estimated reaction heats for both processes fall in all cases within the observed activation energies of reaction.

The order of reactivity for double-bond attack was 1:3 > mono or 1:4, whereas for α-methylenic attack it was 1:4 > 1:3 > mono.

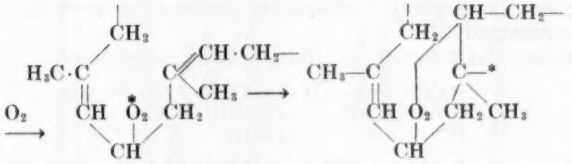
Superficially, in a reaction of reasonable chain length, the position of initial attack, determining the nature of only a small percentage of product, would be of little importance. However, in a system involving chain-transfer agents a long reaction chain is replaced by a number of short chains, involving reaction of the same number of molecules. The number of initiation steps must thereby be multiplied, and the nature of the initiation product assumes an increasing

importance. Accelerators involving functional thiol groups are probably chain transfer agents.

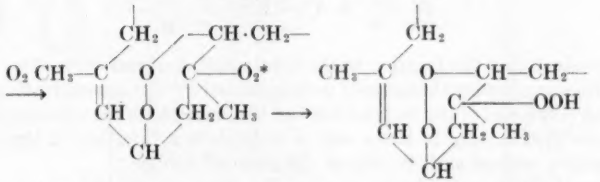
Experiments using squalene[3] as a model substance have shown that peroxidation of rubber probably involves peroxides of two types—the oxidation involving initially the formation of an α-methylenic peroxide radical, which reacts intramolecularly at the double bond, which then peroxidizes further forming a hydroperoxide. Kinetic data in conjunction with this constitutional evidence have led Bolland and Gee to postulate a reaction chain of the following type:



Initiation (A)



(B) Intramolecular peroxide radical (C)

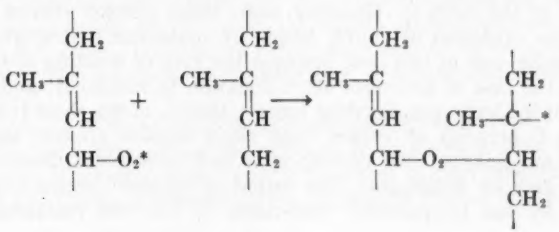


Formation of diperoxide and new hydrocarbon radical (D)

Several aspects of this mechanism command immediate attention: First, at each step where an unpaired electron appears on carbon, competitive reaction for oxygen, sulfur, or a hydrogen atom must occur.

$$R_3—C^* + O_2 \longrightarrow R_3C—O_2^*$$
$$R_3—C^* + Sx \longrightarrow R_3C—Sx^*$$
$$R_3— —C^* + AH \longrightarrow R_3—CH + A^*$$

Secondly, there appears to be a reasonable chance that inter- rather than intramolecular dialkyl peroxide formation can occur leading to an oxygen crosslinkage.



Thirdly, the intervention of an antioxidant or chain transfer agent at the successive stages in chain development leads to oxygenated products which differ in structure and stability.

We must now attempt to set up a variety of model circumstances and predict the behavior to be anticipated in each case.

Assume that we have a sample of vulcanized rubber containing a sufficient number of peroxidic groups, formed in the vulcanization process, to initiate further oxidation chains. Assume also that there is present an antioxidant which functions by a mechanism:

$$\begin{matrix} \text{R—}^* + AH \rightarrow RH + A^* \\ 2A^* \qquad\quad \rightarrow A_2 \end{matrix}$$

and a chain transfer agent, say unreacted accelerator of the thiol type, functioning by a mechanism:

$$\begin{matrix} R_1^* + \text{HSR} \rightarrow R_1H + \text{R—S}^* \\ R_2H + \text{R—S}^* \rightarrow \text{R.SH} + R_2^* \end{matrix}$$

where R_1— and R_2— indicate variations in the bond energy of the C—H bond produced or ruptured.

Alternatively, chain transfer could occur by the mechanism:

$$\begin{matrix} \text{R.OO}^* + \text{R}'\text{—SH} \rightarrow \text{R.OOH} + \text{R}'\text{—S}^* \\ \text{R}'.\text{S}^* + \text{RH} \quad\quad \rightarrow \text{R.OOH} + \text{R}^* \\ \text{R}^* + \text{O}_2 \quad\quad \rightarrow \text{R.O}_2^* \end{matrix}$$

There is, of course, a further possibility of destruction of radical chains:

$$\begin{matrix} \text{R}'\text{—S}^* + A^* \rightarrow \text{R}'\text{S—}A \\ 2\text{R}'\text{—S}^* \quad\quad \rightarrow \text{R}'\text{—S.S.—R}' \end{matrix}$$

It is evident that the fraction of the total number of radical centers occurring in the rubber molecules themselves is determined by the concentration and rate of reaction (lifetime) of the radical derived from the chain transfer agent. Also, the volume distribution of these active radicals is a function of the life of the chain transfer radical and its rate of diffusion in rubber.

The total number of chains growing is a function of the antioxidant concentration, and the nature of the intermediate oxidation products depends on the relative speeds of hydrogen atom transfer to radicals *A*, *B*, *C*, and *D* in the preceding scheme.

If the accelerator-antioxidant initiates reaction by a process leading to radical *A* in the preceding scheme and this gives rise to peroxide radical *B*, then two possible reactions of radical *B* must be considered. It may acquire a hydrogen atom forming the peroxide molecule, or it may form a bridged peroxide ring leading to a radical of type *C*.

In the former the peroxide formed can decompose without chain scission, and it should be possible to have oxygen uptake without marked physical deterioration of the rubber. However, some chain scission always occurs as a result of the oxidation of double bonds by molecular hydroperoxides. The oxygen uptake rate in this case involves the rate of reaction of oxygen with radical *A*, the rate of hydrogen atom donation to radical *A*, and the rate of oxidation of the hydrogen donating species, that is, of the chain transfer agent.

If type *C* peroxide is formed, then chain scission appears together with transient cross-linkage, and development and subsequent decay in physical properties may be anticipated; the extent of opposed phenomena is largely controlled by the temperature coefficients of the two reactions. Type *D*

peroxide would be expected to decompose more readily and with even more drastic degradation.

To disentangle the complex sequence of events outlined, it seems desirable to undertake stimultaneous experimental investigations of the kinetics of the reactions involved and the changes in physical properties of the rubber and, using this technique, to study the effect of additions of systematic series of reagents having varying hydrogen atom donating properties, giving rise to radicals of varying longevity.

EXPERIMENTAL

Apparatus.—The apparatus, which is the subject of a patent application, is shown diagrammatically in Figure 1.

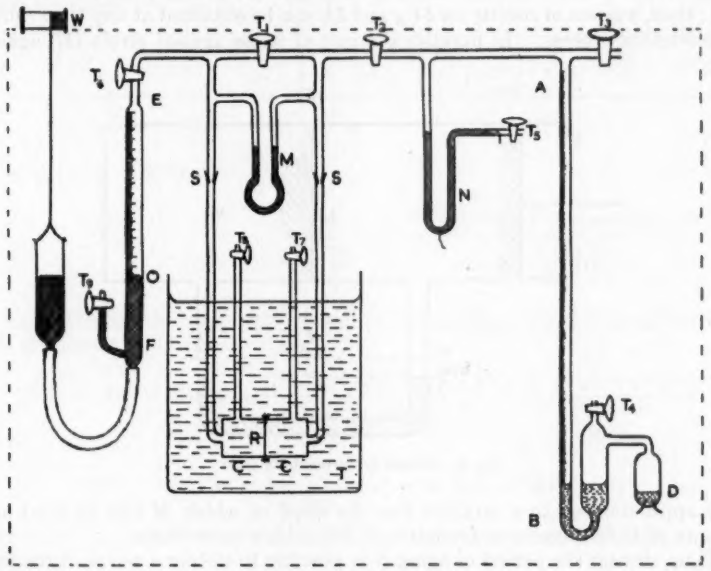


FIG. 1.—Diagram of apparatus.

The rubber sample, *R*, in the form of a thin disk 1.25 inches in diameter, is clamped between the flanged cylinders, *C*, so that an area 1 inch in diameter is exposed in the form of a diaphragm across the cylinder, *CC*. The cylinder assembly is attached to the remainder of the apparatus by means of two ground joints, *SS*, and can be surrounded by a thermostat bath, *T*. The latter is filled with a mobile silicone fluid and is equipped with stirrer, heater, and Thermistor temperature control unit[4]; this allows the temperature of the bath to be controlled with a high degree of accuracy and to be set readily at any desired level. The apparatus is housed in an air thermostat controlled accurately at 34° C.

The oxygen absorption system is of the constant-pressure type. Absorption of oxygen by the rubber causes the contacts in manometer tube *N* to break. This operates a Thyratron relay causing a current to pass through electrolyte in vessel *D*, and the gas generated forces the mobile silicone liquid in tube *AB*

upwards until the pressure in the apparatus is restored. Thus the rise of liquid in tube AB is a direct measure of the oxygen absorbed by the sample.

The mechanical properties of the membrane can be obtained at any time during oxidation by using the following procedure:

Tap T_2 is closed and T_6 opened. The mercury level in tube EF is then adjusted to its zero position, and the equal volumes of gas on either side of the membrane are isolated from each other by closing tap T_1. An excess pressure can then be generated on the left-hand side of the membrane by raising the mercury level in tube EF, causing the membrane to be deformed into a spherical cap, the pressure difference, δP, being determined by manometer tube M.

Equation 6 expresses the volume displacement of the membrane, δV_R, in terms of the volume displacement in tube EF (δV_0) and pressure difference (δP); thus, a series of results for δV_R and δP can be obtained at any time during the oxidation process. In practice the plot of stress against strain (δP against

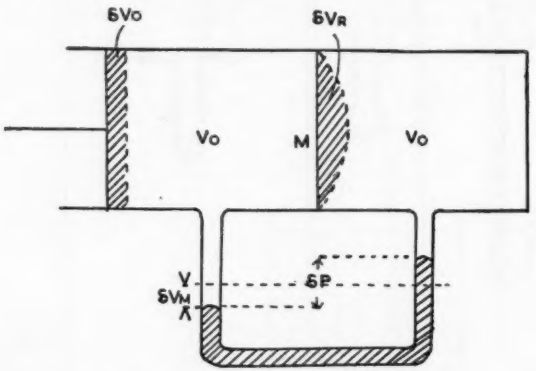


FIG. 2.—System for stress-strain cycle.

δV_R) approximated to a straight line the slope of which M can be used as a measure of the stiffness, or modulus, of the rubber membrane.

Thus, during the period of aging it is possible to obtain a series of readings directly relating oxygen absorption (in ml./gram) to stress-strain properties (modulus) ($\delta P/\delta V_R$).

Derivation of δV_R.—The system is shown diagrammatically in Figure 2:

V_0 = the volume on either side of the membrane when taps T_1, T_2, T_7, and T_8 are closed, and the mercury level in EF is at zero. (In practice these volumes are arranged to be equal)
δV_0 = the volume displacement of the mercury in tube EF
δP = the pressure difference as determined by manometer M
δV_M = the change in volume due to movement of the mercury in manometer M
δV_R = the volume displacement of the rubber disk
P_0 = the pressure in the apparatus, normally atmospheric
$\delta P'$ = the increase in pressure on left-hand side
$\delta P''$ = the increase in pressure on right-hand side for volume displacement δV_R

For the left-hand side:

$$P_0V_0 = (P_0 + \delta P')(V_0 - \delta V_0 + \delta V_R + \delta V_M) \quad (1)$$

and for the right-hand side:

$$P_0V_0 = (P_0 + \delta P'')(V_0 - \delta V_R - \delta V_M) \text{ and} \quad (2)$$

$$(P_0 + \delta P') - (P_0 + \delta P'') = \delta P \quad (3)$$

From Equations 1, 2, and 3:

$$\frac{P_0V_0}{(V_0 - \delta V_0 + \delta V_R + \delta V_M)} - \frac{P_0V_0}{(V_0 - \delta V_R - \delta V_M)} = \delta P \quad (4)$$

which simplifies to:

$$\delta V_R = \frac{\left(\delta V_0 - 2V\delta_M + \frac{2P_0V_0}{\delta P}\right) \pm \sqrt{4\left(\frac{P_0V_0}{\delta P}\right)^2 + \delta V_0^2 + 4V_0^2 - 4V_0\delta V_0}}{2}$$

or

$$2\delta V_R = \left(\delta V_0 - 2\delta V_M + \frac{2P_0V_0}{\delta P}\right) \pm \frac{2P_0V_0}{\delta P}\left\{1 + \frac{\delta V_0^2 + 4V_0^2 - 4V_0\delta V_0}{4\left(\frac{P_0V_0}{\delta P}\right)^2}\right\}^{1/2} \quad (5)$$

Using the negative sign and expanding to one term, which is quite justified with the present numerical values:

$$2\delta V_R = \delta V_0 - 2\delta V_M + \frac{2P_0V_0}{\delta P} - \frac{2P_0V_0}{\delta P} - \frac{1}{2}\frac{\delta V_0^2 + 4V_0^2 - 4V_0\delta V_0}{\frac{2P_0V_0}{\delta P}}$$

$$= \delta V_0 - 2\delta V_M - \frac{1}{4}\frac{\delta P}{P_0V_0}(\delta V_0^2 + 4V_0^2 - 4V_0\delta V_0)$$

Then since $V_M = \alpha P$ where α us half the cross-sectional area of the manometer tube M:

$$\delta V_R = \frac{\delta V_0}{2} = \left(\frac{\delta V_0^2 + 4V_0^2 - 4V_0\delta V_0}{8P_0V_0} + \alpha\right)\delta P \quad (6)$$

Equation 6 can be expressed conveniently as a series of curves relating δP and δV_R for given values of δV_0 and atmospheric pressure (Figure 3), and the successive values of δV_R can be obtained readily.

Procedure.—The procedure adopted during a typical experiment is briefly as follows:

The rubber sample, cut from suitable thin molded sheet approximately 0.025 inch thick, was clamped into position, and the cell assembly, *S*, *C*, *C*, *S*, was then attached to the main apparatus by the ground joints, *SS*. The sample thickness was chosen so that oxygen uptake by the rubber and not diffusion rate was the governing factor. Nitrogen was swept through the apparatus entering through tap T_3 and leaving by taps T_7, T_8, and T_9; during this step, the liquid level in the tube *AB* was repeatedly raised and lowered by applying

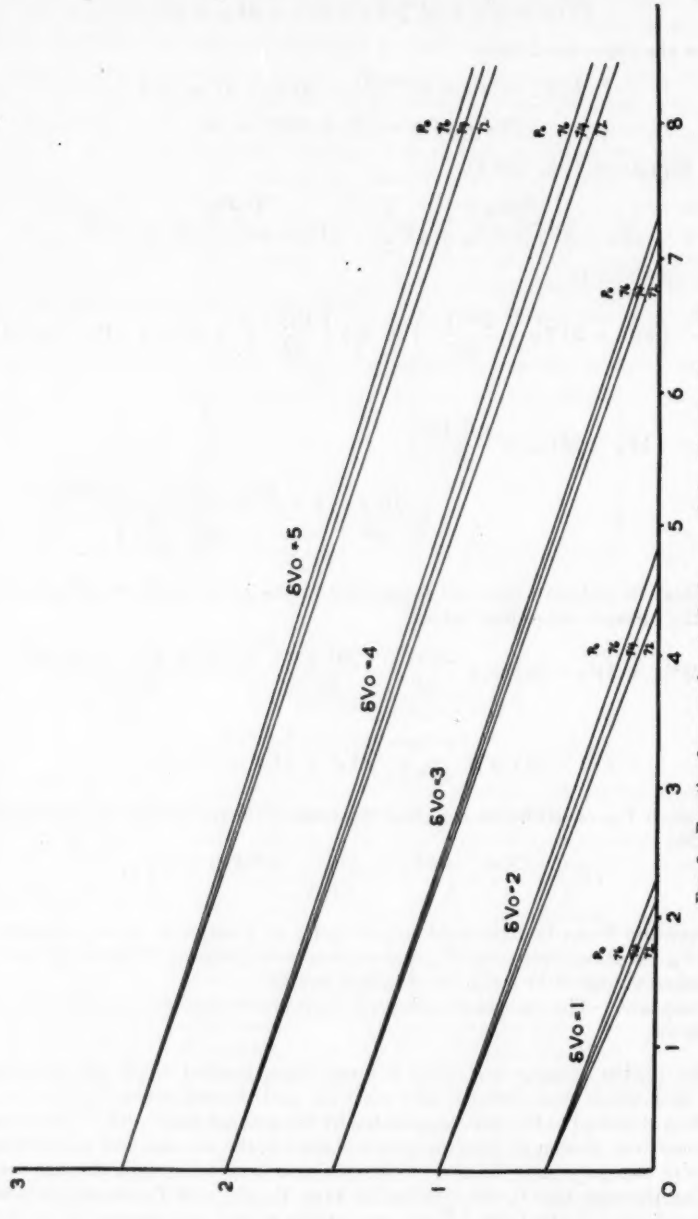


FIG. 3.—Equation 6 expressed as standard curves relating δV_R, δP, δV_0 and P_a.

pressure through tap T_4. After a few minutes the supply of nitrogen was cut off by closing trap T_3 and the thermostat bath was placed in position.

After adjusting the mercury level in EF to zero position, so that the volume of gas on either side of the membrane was equal, taps T_1, T_2, T_7, and T_8 were closed and the rubber was passed through an elastic cycle by raising the mercury level in EF in steps. Readings were made of the volume change, δV_0, in EF and the pressure difference, δP, in manometer M, and in this way a series of δV_0 and δP readings with increasing δP were obtained.

The nitrogen was then replaced by oxygen through tap T_3, using the same technique as was used to fill the apparatus with nitrogen initially, and the mercury in EF was adjusted to its zero position. Then by closing taps T_3, T_4, T_7, and T_8 and switching on the Thyratron relay, equilibrium was reached in the apparatus with the liquid level in AB at a conveniently low position. This reading was arbitrarily taken as zero absorption. Finally taps T_5 and T_6 were closed to isolate the apparatus completely from changes in atmospheric pressure.

Oxygen absorption was measured by the rise of liquid level in AB and stress strain properties, at intervals, by taking the sample through a series of elastic cycles as indicated above.

RESULTS

A summary of the results of an investigation into the aging characteristics at 120° C of four different rubber vulcanizates containing different accelerators and antioxidants is given in Table I. Duplicate measurements were made in each case.

Figure 4 shows the oxygen absorption to time relationship for duplicate runs on each stock.

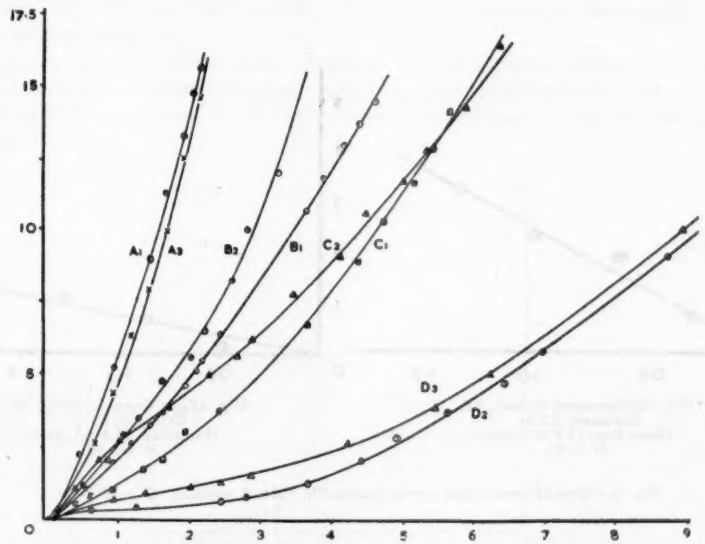
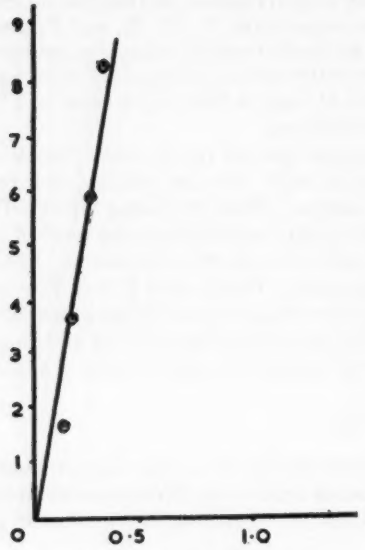
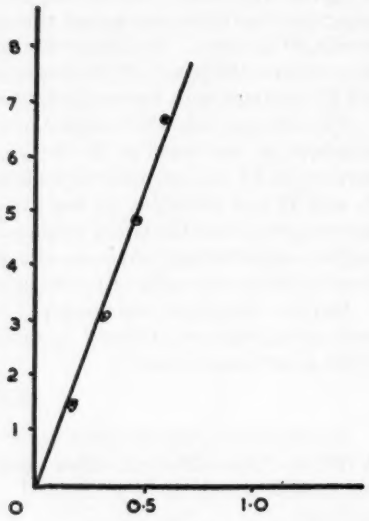


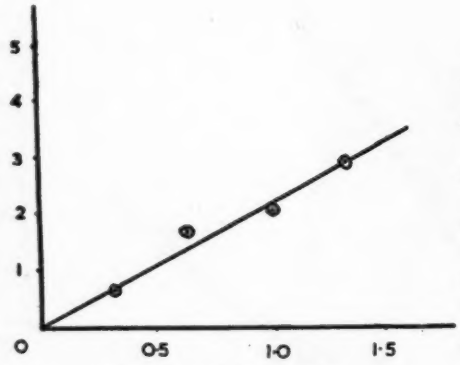
FIG. 4.—Rate of oxygen absorption. Duplicate samples of four stocks shown in Table I.



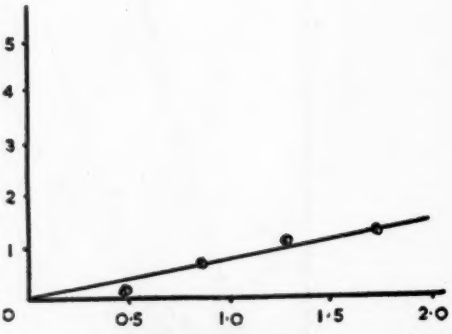
δV_R (Displacement of Disc), Ml.
Exposure, nil
Absorption, nil
M = 26



δV_R (Displacement of Disc), Ml.
Exposure, 2 hr.
Absorption 3.0 ml./gram
M = 10.7



δV_R (Displacement of disc), Ml.
Exposure, 5.5 hr.
Absorption, 12.9 ml./gram
M = 2.1



δV_R (Displacement of Disc), Ml.
Exposure, 7 hr.
Absorption 19.8 ml./gram
M = 0.80

FIG. 5.—Typical stress-strain curves (sample C_1, Table I, modulus, $M = \delta P/\delta V_R$).

TABLE I

AGING CHARACTERISTICS OF FOUR STOCKS

Stock formula	Parts A		B		C		D	
Pale crepe	100		100		100		100	
Zinc oxide	3		3		3		3	
Stearic acid	0.5		0.5		0.5		0.5	
Sulfur	2.0		3.0		2.5		2.5	
Tetramethylthiuram disulfide	0.375		—		—		—	
Diphenylguanidine	—		0.5		—		—	
Mercaptobenzothiazole	—		—		0.6		0.6	
Phenyl-β-naphthylamine	—		—		—		0.75	
Vulcanization (min.)	15 at 126° C		60 at 141.5° C		50 at 134° C		50 at 134° C	
Sample	A_1	A_2	B_1	B_2	C_1	C_2	D_2	D_3
Sample weight (gram)	0.34	0.30	0.33	0.34	0.37	0.38	0.37	0.33
Oxygen absorption rate (cc./g.hr.)								
At 5 cc/g. level	7.23	7.35	3.31	3.19	2.32	2.12	1.68	1.73
At 10 cc./g. level	8.75	8.75	3.90	4.18	3.45	3.37	2.10	1.90
Time (min.) for modulus to decay								
50% ($t_{1/2}$)	35	30	40	35	100	85	235	170
75% ($t_{1/4}$)	50	50	59	63	195	190	470	420
Oxygen absorption (cc./g.)								
At $t_{1/2}$	2.3	1.7	1.2	1.2	2.2	3.3	1.5	1.4
At $t_{1/4}$	4.1	3.3	1.9	2.4	5.7	6.9	7.3	6.3

Figure 5 illustrates the type of stress-strain ($\delta P/\delta V_R$) relationship obtained with one specimen (sample C_1) after four periods of aging.

Figures 6 and 7 illustrate the type curves obtained relating modulus (average $\delta P/\delta V_R$) with time and modulus with oxygen absorption, the sample used in each case being C_1.

Similar sets of curves were obtained for all samples tested. In every instance sample thickness was maintained at approximately 0.025 inch, and all samples had been stored in the dark at 25° C for at least a week before being tested.

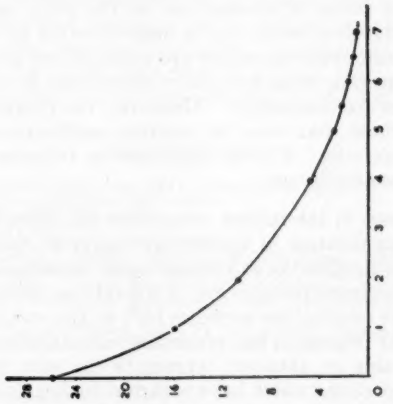


FIG. 6.—Typical curve relating decay of modulus to time of oxidation. Sample C_1, Table I.

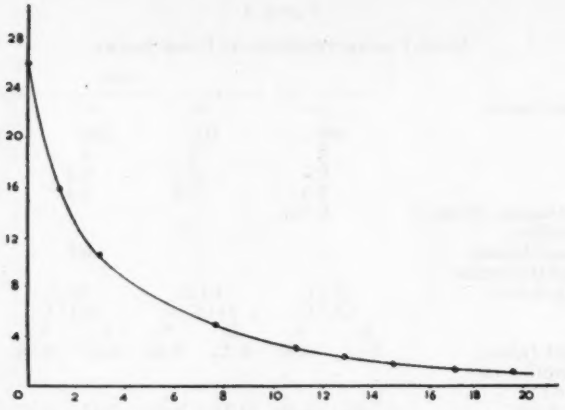


FIG. 7.—Typical curve relating decay of modulus to quantity of oxygen absorbed. Sample C_1, Table I.

Careful examination of all samples tested suggested that oxidation had proceeded in a homogeneous manner throughout the body of the rubber.

DISCUSSION

It has generally been concluded that for results to be of most value, oxygen absorption experiments must be carried out at constant pressure and under carefully controlled conditions in respect to sample prehistory, exposure to light, and temperature. The method outlined here is no different in principle, in these aspects, from several others previously described in the literature. It is novel, however, in respect to the following points:

1. Measurement of deterioration in stress-strain properties can be carried out on the same sample and under the same conditions as is measurement of oxygen absorption. This eliminates a major criticism of many correlations of oxygen absorption with deterioration in physical properties made in the past[5].
2. A progressive series of correlations on the same sample is possible as aging proceeds, as measurements can be made as often as desired.
3. The stress-strain determinations are made at low elongations and under two-dimensional stressing, thus secondary effects due to excessive orientation of the rubber chains are minimized. Moreover, the elongations employed are more in line with those that occur in practical applications than are the conventional test elongations. This is important in bringing testing into closer relation with service conditions.

The actual stresses in the rubber membrane are difficult to determine with accuracy, and the application of the kinetic theory of rubber elasticity to the type of deformation involved is at present under investigation.

For practical purposes, the concept of a modulus value as the slope of the average straight line relating the pressure (δP) to the volume movement of the rubber sample (δV_R) (Figure 5) has proved of value in interpreting results.

The modulus value so obtained represents the sum of chain-scission and structure-forming reactions which have occurred during aging and, in its present form, the method cannot separate these types of processes along the lines indi-

cated by the stress relaxation investigation of Tobolsky and co-workers[6]. This does not reduce the value of the information gained from direct correlation of stress-strain properties with oxygen absorption, but it may limit interpretation of the data at a later stage when detailed consideration as to the nature of the chemical reactions involved is important.

Figure 4 shows that for a period at 120° C, during which the physical properties of the several rubbers had deteriorated to a very marked extent, the oxygen absorption proved to be autocatalytic in nature. This draws attention again to the fact that, under high temperature conditions, much of the damage to essential rubber properties seems to be done during the very early stages of oxidation, even in stocks which are well protected by antioxidant.

Reproducibility of measurements has proved to be reasonably good, and since the work described here was completed, further improvements in technique have been made. Until more work has been done on the effect of various factors, some limitations must be placed on the data. However, the summary in Table I demonstrates the capacity of the test procedure to define clearly the aging characteristics of four different stocks.

The data also illustrate the very important role of vulcanization systems in determining the aging characteristics of a rubber sample and the inaccurate conclusions that could result if these characteristics were deduced from oxygen absorption studies only. For example, although the time required to attain a give percentage of deterioration in physical properties is the same for stocks *A* and *B*, rate of oxygen absorption is much higher in the case of stock *A*. Stock *C* appears to possess superior aging characteristics to stock *B* largely because a higher proportion of the oxygen absorbed seems to be directed into "inactive" combination, although some reduction in rate of absorption is noted as well. Mercaptobenzothiazole has long been recognized as an excellent antioxidant, as well as accelerator, and these results emphasize the possible similarity of role played by this accelerator and the structurally similar antioxidant material, mercaptobenzimidazole, whose function as a deactivator was outlined by Le Bras and coworkers[7].

The role of phenyl-β-naphthylamine in reducing the rate of oxygen uptake is shown by comparison of the data given for stocks *C* and *D*.

The results so far obtained have been sufficiently encouraging to warrant undertaking a more detailed program, and investigations along the lines indicated earlier in this paper are now in progress. Further consideration is being given also to modification of the apparatus to make it more robust and easy to operate and to correlate the information obtained for use with data obtained by other test methods.

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STOICHIOMETRY OF VULCANIZATION WITH SULFUR *

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INTRODUCTION

In the study of vulcanization with natural rubber and other polymers of relatively high chemical unsaturation, it has always been difficult to represent the vulcanization process molecularly because of the complexity of the sulfur-polymer reactions. To circumvent this difficulty, reactions of small olefin molecules with sulfur have often been studied to obtain this molecular insight.

Some investigators have resorted to cross-linking the polymer with agents other than sulfur to characterize the network for comparisons with physical properties. By cross-linking rubber molecules with diazo compounds, which add quantitatively to the olefin bond, Flory[1] has characterized the network so formed in a molecular manner and correlated the degree of cross-linking with physical properties. When correlating physical properties with degree of cross-linking in butadiene-styrene polymers, others[2] have cross-linked the polymer as a final step in the polymerization process.

When a polymer of low unsaturation is used, many of the experimental difficulties are eliminated or reduced, and a more reliable stoichiometric picture of the phenomenon can be obtained. The emphasis in this work is placed on the chemical combination of sulfur with polymer rather than on any correlation with physical properties, and rests upon the "dimensions" of swollen polymer networks as related to total combined and organically combined sulfur.

The low unsaturation of Butyl rubber[3] makes it possible to satisfy all the potential points of cross-linkage while still possessing a network that is soft and elastic. In actual practice, there probably is a small percentage of the reactive sites or points of unsaturation disposed in such a way that they cannot approach an active site in another molecule. Experimentally, however, one can obtain a "maximum" state of vulcanization where further vulcanization time or additional sulfur and accelerator do not contribute further to additional cross-linkage. This feature is utilized in the present investigations.

EXPERIMENTAL PROCEDURES

The Butyl rubber used in this study was commercial GR-I. It possessed a viscosity-average molecular weight (from the intrinsic viscosity in diisobutylene) of 320,000 and a mole percentage unsaturation by ozonolysis[4] of 0.89 per cent. This polymer was compounded in a nonpigmented formulation with five accelerators derived from dithiocarbamic acid, but for the sake of brevity only the two accelerators shown in Table I will be discussed here.

Since tellurium is quadrivalent, four dithiocarbamate radicals are attached to it in comparison with the thiuram, which is made up of two dithiocarbamate

* Reprinted from the *Journal of Polymer Science*, Vol. 6, No. 3, pages 331–349, March 1951.

TABLE I

Compound	1	4
Butyl	100	100
Zinc oxide	5	5
Tetramethylthiuram disulfide	1	—
Tellurium diethyldithiocarbamate	—	1.55
Sulfur	2	2

radicals. Therefore, it was considered that one mole of thiuram was equivalent to one-half mole of tellurium compound, and the quantities shown in Table I are added in this ratio.

In the body of the paper, the long chemical names for the accelerators are frequently abbreviated according to the following scheme:

Tetramethylthiuram disulfide	TMTDS
Tellurium diethyldithiocarbamate	TDEDC

To obtain more accurate times of the vulcanization reaction and also to obtain temperatures as high as 400° F, a special electrically heated press was designed. The moving parts of a Mooney viscometer were removed, and a special micromold was inserted in the top and bottom platens; thus with the mold attached to the platens, samples could be inserted or removed and the press closed or opened in five seconds. Electrical ring heaters on constant and intermittent heat allowed control of temperatures to about ± 2° F. Samples were vulcanized as thin slabs 2 × 2.5 × 0.030 inches at five temperature levels: 250, 275, 300, 350, and 400° F. The time of cure was taken between the time when the press was closed to the point at which the sample was plunged into ice water after rapid removal from the press. Mold lubrication with Silicone oil eliminated sticking and facilitated this rapid removal. After vulcanization, the state of cure was determined by equilibrium volume swelling in cyclohexane at 25° C.[5] This method yields more reliable indications of the extent of cross-linking at low states of cure than does extension modulus.

TIME, TEMPERATURES, AND THE STATE OF VULCANIZATION

Cure curves for the tetramethylthiuram disulfide-accelerated compound are given in Figure 1 for the five temperatures. Curves for the three lower

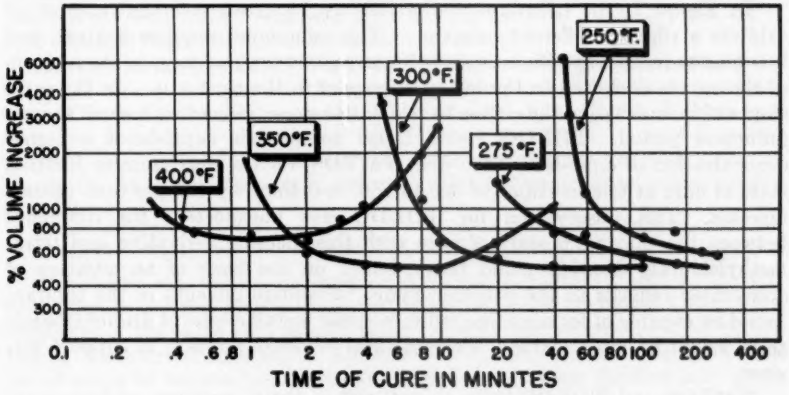


FIG. 1.—Tetramethylthiuram disulfide acceleration.

temperatures are similarly shaped curves (but displaced to the left as temperature increases) which descend to an apparent limiting value of 500 per cent volume increase. In considering these and following curves it must be kept in mind that the lower swelling values indicate a higher state of cure or increased concentration of cross-links, and that the general shape of the curves is the inverse of the usual cure curve, where modulus is used as the criterion of the state of vulcanization. When a temperature of 350° F is approached, the first indications of reversion become apparent for. on extended vulcanization, the effective concentration of cross-links decreases to a point of 1000 per cent volume increase after 40 minutes. At 400° F, the reversion tendencies have become so drastic that they have effectively reduced the maximum state of cure. As shown in the curve for this temperature, 700 per cent volume increase appears as the limiting cure state, after which reversion occurs so rapidly that after 10 minutes of cure a state approaching solubility has been reached.

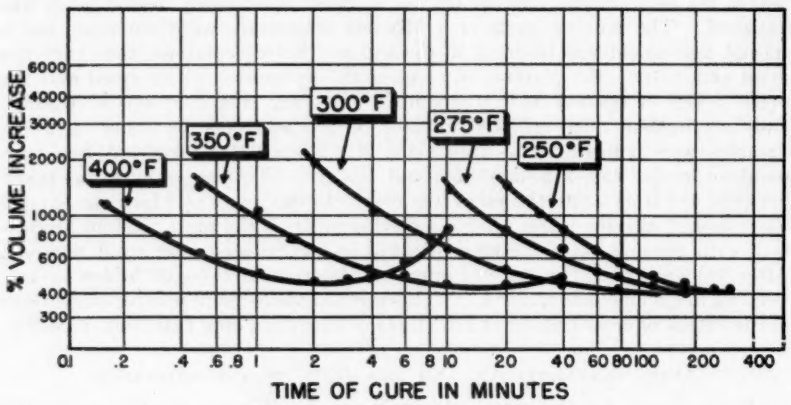


FIG. 2.—Tellurium diethyldithiocarbamate acceleration.

In Figure 2, the tellurium diethyldithiocarbamate-accelerated compound exhibits a slightly different behavior. This compound requires a great deal less time to reach a specific cure state for any given temperature, so the position of the curves is shifted to the left with respect to the time axis. In the early stages of vulcanization the curves have a flatter slope, indicating a much shorter induction period. TDEDC yields Butyl compounds capable of a higher concentration of cross-links than does TMTDS, for the maximum or limiting state of cure at temperatures of 300 to 250° is defined by 400 per cent volume increase. This observation for TDEDC was unexpected; the difference between the maximum state of cure with this metallic derivative and tetramethylthiuram disulfide could be explained on the basis of an addition of accelerator radicals to the polymer chain. Disulfide linkages in the thiuram would be capable of forming free radicals, while metallic salts of dithiocarbamic acids would be more stable. Experimental evidence appears to support this view.

TMTDS and TDEDC were mixed with a Butyl polymer of higher un-

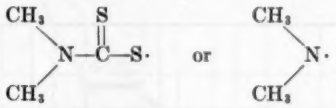
saturation than the commercial GR-I to increase the possibility of radical addition. The proportions by weight are shown in the following table:

Component	1	2	3
Butyl (unsaturated 2 mole-%)	100	100	100
Zinc oxide	5	5	5
TMTDS	3	—	—
TDEDC	—	4.5	—

Mixture 3 was used as a control and all compounds were heated in a press for 30 minutes at 300° F. The samples were then extracted with methylethyl ketone for 48 hours to remove uncombined accelerator fragments. Combined nitrogen and combined sulfur determinations were made on the extracted compounds, and these are tabulated below in weight percentage values:

Element	1 (TMTDS)	2 (TDEDC)	3 (Control)
Nitrogen	0.05%	0.02%	0
Sulfur	0.16%	0.04%	0

Compound 1, containing the thiuram disulfide, shows distinctly more combined nitrogen and sulfur than does compound 2. The control with no accelerator has no combined sulfur or nitrogen. The TMTDS compound exhibited cross-linking; about 80 per cent of the sample existed in a very loose network structure. These analytical results explain the fact that the tellurium compound, in the ordinary vulcanization process with elemental sulfur, is a more efficient accelerator than the thiuram disulfide. The thiuram accelerator containing the disulfide linkage decomposes more readily so that radicals (such as these below) may enter into the chain at potential points of cross-linkage.



If this did occur at an occasional active point along the chain, those sites would lose their cross-linking potentialities, and, in effect, reduction in polymer unsaturation would result. Rehner and Holowchak[6] cite some data on the extractability of accelerators with methylethyl ketone; these data show that the 0.16 per cent sulfur remaining after heating mixture 1 is well in excess of that expected from residual unextracted accelerator.

Another advantage of TDEDC over TMTDS is the marked resistance to vulcanizate reversion observed in compounds containing the tellurium derivative. The vulcanization curves at 350 and 400° F in Figure 2 show how reversion is retarded. At 400° F network has reverted to only 800 or 900 per cent volume increase, compared to 2000 per cent for the 400° curve in Figure 1. At 350° F, the reversion for the TDEDC acceleration is also greatly reduced.

COMBINED SULFUR

Paralleling the volume swelling experiments of Figures 1 and 2, the vulcanization course was also followed by measurements of combined sulfur, using remnants of the same thin sample slabs. Before the volume swelling experiments, the vulcanized samples had been extracted with methylethyl ketone for 16 hours to remove free sulfur and accelerator. Thus the first step in the determination of combined sulfur according to Rehner and Holowchak[6] has

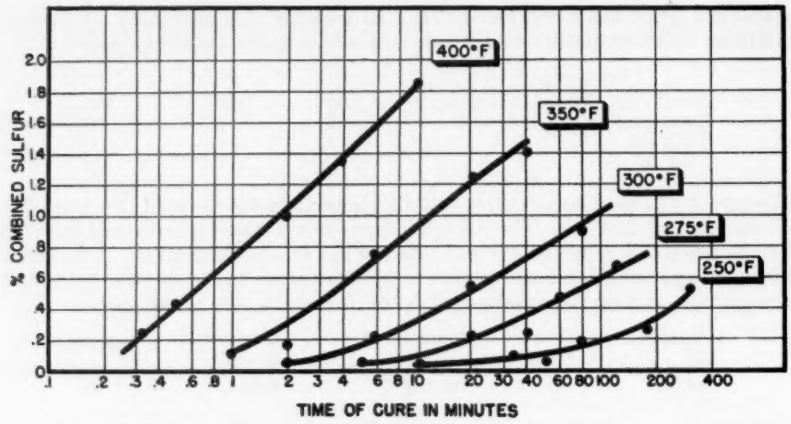


FIG. 3.—Combined sulfur *vs.* time of vulcanization. Tetramethylthiuram disulfide acceleration.

been completed, and the sample can be directly oxidized in the Braun Shell apparatus. Small quantities of combined sulfur (after conversion to sulfate) were determined turbidimetrically by the method of Zahn.[7]

The results of the combined sulfur analyses of the two compounds listed in Table I are shown in Figures 3 and 4. In general both accelerators show similar behavior as vulcanization progresses. At higher and higher tempera-

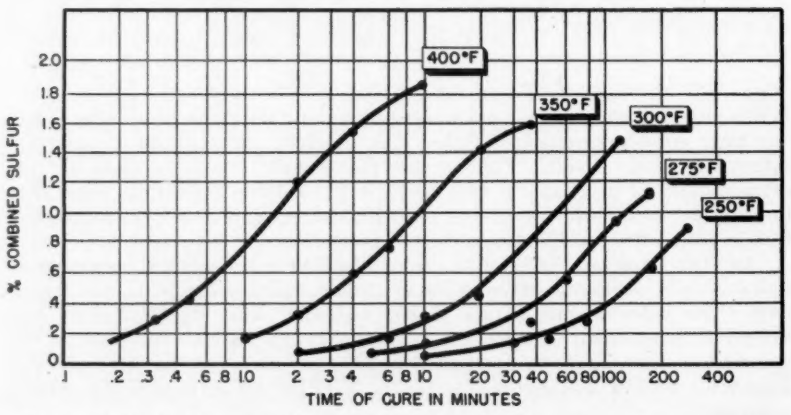


FIG. 4.—Combined sulfur *vs.* time of vulcanization. Tellurium diethyldithiocarbamate acceleration.

tures there is a steady increase in the percentage of combined sulfur by weight present in the vulcanizate. It will be recalled that in the volume swelling–vulcanization time curves, the degree of cross-linking began to decrease on approaching temperatures of 350 to 400° F. In Figures 3 and 4, combined sulfur continues to increase at the higher temperatures, even though the reversion process has been shown to have set in. With TDEDC, higher com-

bined sulfur is encountered at the lower temperatures, reflecting the apparently higher degree of cross-linking ultimately obtained with this compound.

Under the conditions of vulcanization, sulfur is combined in two general forms: organically combined sulfur and sulfur in the form of zinc sulfide. The latter presumably originates from the reaction of zinc oxide with hydrogen sulfide formed during vulcanization. To obtain a true stoichiometric picture of vulcanization, these two forms of combined sulfur must be differentiated. This was accomplished by reacting the unchanged zinc oxide with oleic acid (in a swollen sample), followed by extraction of the zinc oleate. After extraction, only zinc in the form of sulfide remained, and the sample was then analyzed for zinc and converted to equivalent weight of inorganically combined sulfur.

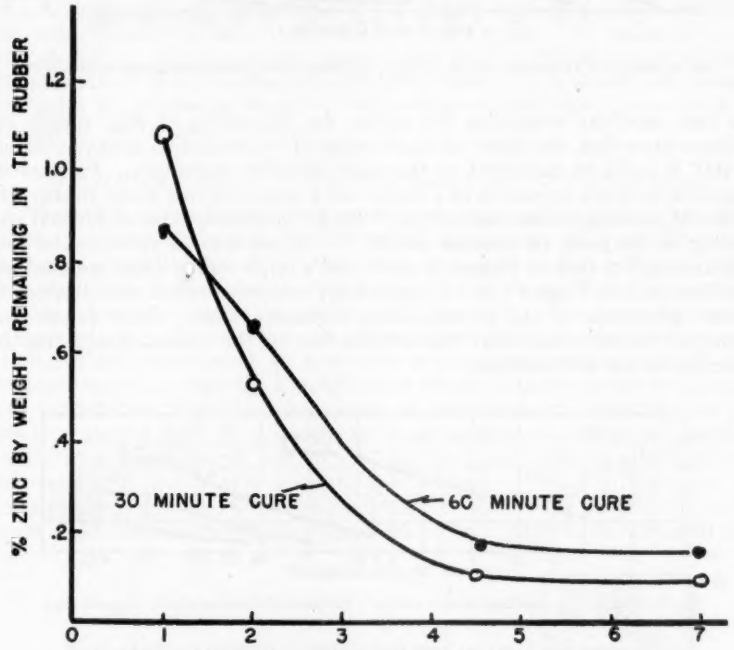


FIG. 5.—Extraction of zinc oxide from Butyl at two levels of vulcanization. Abscissa: hours, digestion in naphtha solution of oleic acid.

In detail, appropriate samples of the vulcanizate which had first been analyzed for combined sulfur were heated in a 50–50 volumetric mixture of naphtha and oleic acid for approximately 16 hours. Previous tests indicated that reaction was complete in 8 hours at a temperature of about 93° C, as shown in Figure 5. The rubber sample, which had originally been confined in a filter paper envelope, was then extracted in Soxhlet extractors with benzene, followed by methylethyl ketone to remove the zinc oleate. The samples, thus freed of zinc oxide, were analyzed for zinc by a polarographic method[8].

The results of the zinc analysis, after conversion to the equivalent weight of inorganically combined sulfur, are shown in Figure 6 for the TMTDS

acceleration and in Figure 7 for the TDEDC acceleration. It is readily seen that the marked increase in combined sulfur exhibited during vulcanization at higher temperatures can be explained in part by the increase in zinc sulfide sulfur with increase in reaction temperature. Promotion of zinc sulfide formation at higher curing temperatures would favor reversion, since sulfur combined in this form would be unavailable for polymer cross-linking. With

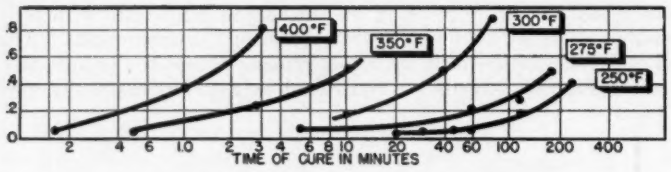


FIG. 6—Sulfur (%) combined as zinc sulfide. Tellurium diethyldithiocarbamate acceleration.

the two reactions competing for sulfur, *i.e.*, formation of zinc sulfide and polymer cross-link, the lower ultimate state of vulcanization always obtained at 400° F could be explained on the basis of sulfur starvation. Polymer degradation does not appear to be a factor, for a sample of raw Butyl rubber with a viscosity-average molecular weight of 305,000 yielded a value of 310,000 after heating in the press 10 minutes at 400° F. From a series of curves of total combined sulfur such as Figures 3 and 4 and a series representing inorganically combined sulfur, Figures 6 and 7, organically combined sulfur was obtained by taking differences of the corresponding ordinate values. Such values were employed for the molecular characterization of the vulcanization reaction discussed in the next section.

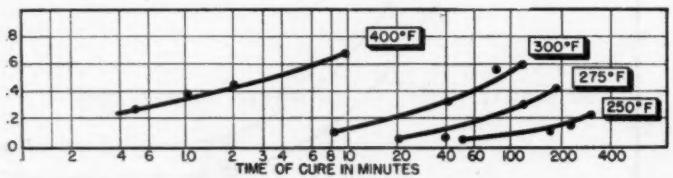


FIG. 7.—Sulfur (%) combined as zinc sulfide. Tetramethylthiuram disulfide acceleration.

MOLECULAR CHARACTERIZATION OF VULCANIZATION

Using a tetrahedron model unit representing a polymer network, Flory and Rehner[9] defined the swelling of the network in terms of the molecular weight of the chain between cross-links, the volume fraction of polymer in the swollen gel, and the molar volume of the solvent. Their relationship is:

$$M_c = -\rho V_1 v_2^{\frac{1}{3}}/[\ln(1 - v_2) + v_2 + \mu v_2^2] \qquad (1)$$

where M_c = molecular weight of chain between cross-links, ρ = density of polymer, V_1 = molar volume of solvent, v_2 = volume fraction of polymer in the swollen gel, and μ = liquid-polymer interaction coefficient.

The parameter, μ, which is characteristic of a given liquid polymer system, can be determined for soluble polymer-solvent systems by osmotic pressure

methods[10]. In order that equation (1) may be applied to the stoichiometry of sulfur cross-linking, a fairly reliable value for μ, between solvent and a network, must be obtained. This is usually accomplished through indirect means. For example, μ for polyisobutylene dissolved in cyclohexane[10] was found to be 0.41 by osmotic pressure measurements; by relating tension at a given degree of elongation to equilibrium swelling in cyclohexane at 25° C. Flory[11] arrived at a value for μ of 0.3 for a Butyl rubber vulcanizate. Doty and Zable[12] used calibrated cross-linked polyvinyl chloride to procure interaction coefficients for a large group of solvents. They assumed that μ for a very loosely cross-linked network would be the same as that obtained from osmotic pressure measurements on soluble polymers. Their work yielded experimental confirmation to the Flory-Rehner equation, for, on calculation, the chain length, M_c, of various polyvinyl chloride gels was essentially the same, for a particular gel, regardless of the solvent in which it was swollen. As intimated in the introduction, a polymer of low unsaturation such as Butyl rubber simplifies the evaluation of an interaction coefficient, because it is possible to define a minimum M_c (molecular weight of chain between cross-links) from which the parameter can be determined.

MOLECULAR WEIGHT OF POLYMER CHAINS BETWEEN CROSS-LINKS

The Butyl rubber used in these experiments was a whole polymer of 320,000 viscosity-average molecular weight[13], which corresponds to a number-average molecular weight[14], M_n, of 175,000. The unsaturation and the chain length between points of unsaturation were determined by ozonolysis[15]. The intrinsic viscosity data after ozonolysis are given in Figure 8. This intrinsic viscosity corresponds to a viscosity-average molecular weight of the degraded chain of 11,300, which corresponds to a number-average molecular weight of 6300. This last figure is, then, the average chain weight between points of unsaturation. Therefore, if careful vulcanization is conducted at a relatively low temperature (below 300° F) a condition is approached for which all points of unsaturation are satisfied, and an average minimum chain length of 6300 for this sample of vulcanizate exists in the network. Figure 9 illustrates how Butyl can be vulcanized to a maximum state of cure. The three curves of this figure reveal that increased quantities of sulfur and TDEDC do not result in an

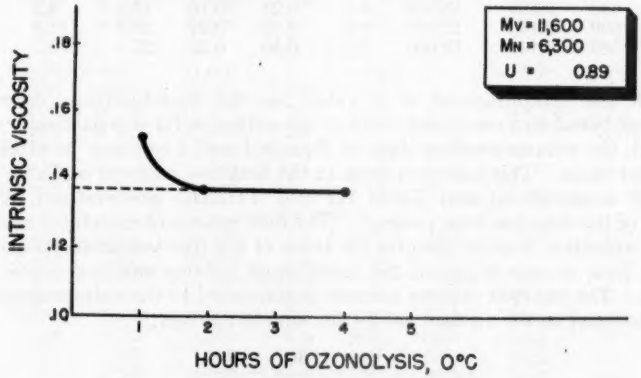


FIG. 8.—Ozonolysis of Butyl polymer used in this study.

ultimately higher concentration of cross-links. The only change affected by the increased dosages of curatives is a more rapid rate of curing at the early stages of the reaction. The maximum state of cure is defined by 400 per cent volume increase for this sample of GR-I. This volume increase corresponds to a volume fraction of polymer, v_2, of 0.2. Now if the value 6300 for M_c is substituted into the Flory-Rehner equation, using 108 cc. as the molar volume of cyclohexane at 25° C, 0.2 for v_2, and 0.915 as the density of the Butyl, μ is found to be 0.35. This value is not far from the value 0.3 obtained with the aid of tension measurements[11].

TABLE II

TETRAMETHYLTHIURAM DISULFIDE ACCELERATION

Time (min.)	Per cent volume increase	v_2 (volume fraction)	M_c (chain length)	$\frac{1}{2}(Mn/M_c)$ (cross-links per average molecule)	Combined S (%)	Organic S (%)	Atoms combined S per average molecule	Atoms organic S per average molecule	Atoms organic S per cross-link
				At 400° F					
¼	950	0.095	26,500	3.3	0.23	—	12.57	—	—
½	750	0.118	18,000	4.86	0.44	0.16	24.02	8.74	1.8
1	720	0.122	16,900	5.18	0.74	0.38	40.41	20.74	4.0
7	730	0.120	18,000	4.86	1.03	0.59	56.3	32.22	6.6
3	870	0.103	23,200	3.77	1.26	0.77	66.8	42.05	11.2
4	1020	0.089	29,500	2.97	1.38	0.84	75.3	45.9	15.5
6	1380	0.073	51,000	1.72	1.6	1.0	87.4	54.6	31.8
10	2800	0.035	161,000	0.5	1.85	1.15	101	62.8	—
				At 300° F					
5	3600	0.027	148,000	0.6	0.16	—	8.74	—	—
8	1100	0.083	39,200	2.22	0.26	0.16	14.2	8.7	3.9
10	690	0.127	16,000	5.47	0.32	0.19	17.5	10.4	1.9
20	540	0.156	10,700	8.58	0.54	0.32	29.5	17.5	2.0
40	500	0.167	9,300	9.41	0.73	0.41	39.8	22.4	2.3
80	490	0.169	9,100	9.62	0.93	0.35	50.2	19.1	2.0
120	500	0.167	9,300	9.41	1.00	0.38	54.6	20.8	2.2
				At 250° F					
50	3000	0.032	160,000	—	0.08	—	4.4	—	—
60	1150	0.080	38,700	2.3	0.12	0.07	6.6	3.8	1.7
80	870	0.103	24,400	3.6	0.18	0.10	9.8	5.5	1.5
120	720	0.122	16,900	5.2	0.22	0.11	12.0	6.0	1.2
180	640	0.135	13,700	6.4	0.28	0.15	15.3	8.2	1.3
240	600	0.143	12,000	6.9	0.38	0.21	20.8	11.3	1.6
300	580	0.147	12,000	7.3	0.50	0.25	27.3	13.7	1.9

With the establishment of a value for the liquid-polymer interaction coefficient based on a maximum state of vulcanization for this particular sample of Butyl, the volume swelling data of Figures 1 and 2 can now be placed on a molecular basis. This has been done in the first five columns of Table II (for TMTDS acceleration) and Table III (for TDEDC acceleration), where a portion of the data has been present. The first column of each table represents the vulcanization time in minutes for three of the five temperatures; adjacent to each time of cure is placed the equilibrium volume swelling in the second column. The per cent volume increase is converted to the volume fraction, v_2, of the polymer in the swollen gel by the simple relation:

$$v_2 = \frac{100}{100 + \%\text{ vol. increase}}$$

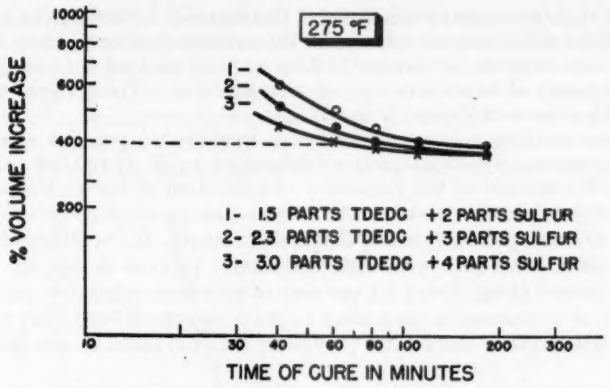


FIG. 9.—Effect of additional curatives on state of vulcanization.

In the fourth column the course of the vulcanization reaction is followed by the reduction in the chain length or molecular weight of the polymer chain between points of cross-linkage. From any crude model or sketch of a cross-link network, it can readily be seen that the number of cross-links is equal to one-half the number of polymer chains. The number-average molecular weight

TABLE III

TELLURIUM DIETHYL DITHIOCARBAMATE ACCELERATION

Time (min.)	Per cent volume increase	v_2 (volume fraction)	M_c (chain length)	$\frac{1}{2}(Mn/M_c)$ (cross-links per average molecule)	Combined S (%)	Organic S (%)	Atoms combined S per average molecule	Atoms organic S per average molecule	Atoms organic S per cross-link
				At 400° F					
¼	790	0.112	19,050	4.6	0.28	0.13	15.28	7.1	1.5
½	640	0.156	10,200	8.6	0.41	0.19	22.38	10.4	1.3
1	500	0.167	9,300	9.4	0.76	0.39	41.50	21.3	2.2
2	470	0.175	8,240	10.6	1.17	0.59	63.9	32.2	3.0
3	470	0.175	8,240	10.6	1.4	0.60	76.5	32.8	3.1
4	500	0.167	9,300	9.4	1.55	—	84.7	—	—
6	570	0.146	11,640	7.5	1.7	—	92.8	—	—
10	870	0.103	23,200	3.8	1.84	—	100.5	—	—
				At 300° F					
2	1850	0.051	91,600	1	0.06	—	8.7	—	—
4	1100	0.083	39,700	2.2	0.14	—	7.6	—	—
10	700	0.125	16,400	5.3	0.28	0.11	15.3	6.1	1.4
20	530	0.159	10,200	8.6	0.47	0.19	25.7	10.4	1.8
40	450	0.162	7,560	11.6	0.85	0.37	46.4	20.2	1.7
80	420	0.192	6,780	12.9	1.24	0.36	67.7	19.7	1.6
120	400	0.200	6,300	13.9	1.48	—	81.0	—	—
				At 250° F					
20	1460	0.064	56,400	1.6	0.09	0.05	4.9	2.7	1.7
30	1100	0.083	39,200	2.2	0.15	—	—	—	—
40	840	0.106	22,200	3.9	0.18	0.13	9.8	7.1	1.8
60	640	0.135	13,700	6.4	0.25	0.19	13.6	10.4	1.6
80	570	0.146	11,640	7.5	0.31	0.22	16.9	12.0	1.6
120	490	0.170	9,100	9.6	0.45	0.28	24.5	15.3	1.6
180	450	0.182	7,560	11.6	0.68	0.40	37.2	21.8	1.9
240	410	0.196	6,600	13.3	0.82	0.42	44.8	22.9	1.7
300	400	0.200	6,300	13.9	0.44	—	—	—	—

of the Butyl polymer used was 175,000; if this figure is divided by the molecular weight of the chain between cross-links, the average number of chain segments per polymer molecule is obtained. This number divided by two gives the average number of cross-links per polymer molecule. These values are listed in the fifth column of Tables II and III.

Because a whole polymer instead of a fractionated polymer was used in this work, tenuous network structures defined by an M_c of 100,000 or so are of little significance due to the possibility of extraction of low molecular-weight species not yet linked to the network. Extraction experiments on vulcanizates from whole Butyl polmer revealed that a chain length, M_c, of 30,000 should not be exceeded if a network with little extractable polymer is desired. At this degree of cross-linking, about 4.4 per cent of polymeric substance was extractable, and, as vulcanization progressed to chain lengths of 7000, only fractional weight percentages of extractable polymeric material could be detected.

COMBINED SULFUR AND THE CONCENTRATION OF CROSS-LINKS

In the sixth and seventh columns of Tables II and III, values of combined sulfur are listed for the various degrees of vulcanization. Some of the numbers are actual experimental values and some are taken from the curves of Figures 3 and 4 at the designated cure times. The values of organically combined sulfur of column 7 are obtained by subtracting the sulfur combined as zinc sulfide from the total combined sulfur for a given time and temperature of vulcanization. Using an average polymer molecular weight of 175,000, the weight per cent of combined sulfur was converted to gram atoms of combined sulfur and gram atoms of organically combined sulfur per average gram-molecule of Butyl for columns 8 and 9, respectively. On dividing atoms of organically combined sulfur by the number of cross-links, values for the atoms of combined sulfur per cross-link are obtained, as shown in the final column.

If attention is first focused on the data for the vulcanization reaction at 250° F in Tables II and III, it is observed that the amount of organically combined sulfur per cross-link remains fairly constant (with few exceptions), and approaches a value of about two atoms of sulfur per cross-link. This constancy is maintained for the most part at reaction temperatures of 275° and 300° F. Plots of atoms of organically combined sulfur per cross-link *vs.* the extent of cross-linking are shown in Figures 10 and 11. As the temperature of vulcanization is increased, a departure from this general constancy is noted. At 350° F, there is a slight but definite trend upward for the amount of sulfur combined per cross-link as vulcanization progresses; this is further emphasized at 400° F, when more drastic reversion or decrease in the concentration of cross-links is observed. These trends are shown under the respective temperatures in Figure 11. For TMTDS acceleration, reversion at high temperatures is more striking, and, as is shown in Figure 10, at 400° F the amount of sulfur combined per cross-link rises sharply with the onset of network degradation. A word of qualification must be made at this point. The high values for combined sulfur per cross-link, noted at 400° in Figure 10, do not lead to the inference that there are twelve atoms of sulfur in a cross-link, but rather that in a more likely mechanism some of the disulfide linkages have been severed, thus decreasing the effective number of cross-links and leaving the sulfur combined in an uncross-linked form.

The instability of the disulfide and polysulfide linkages is well known[16], and these have been reported to undergo thermal decomposition at tem-

peratures above 140° C. In addition, Farmer and Shipley[17] in their study of the reaction of sulfur with olefinic substances did not detect the formation of polysulfide when sulfur and an alkyl disulfide were heated together. In their work with a great number of olefinic materials, sulfur linkages containing from one to six sulfur atoms were obtained, and it is, therefore, of interest that the amounts of combined sulfur in our vulcanization reaction conform to approximately two sulfur atoms per cross-link at temperatures at which no

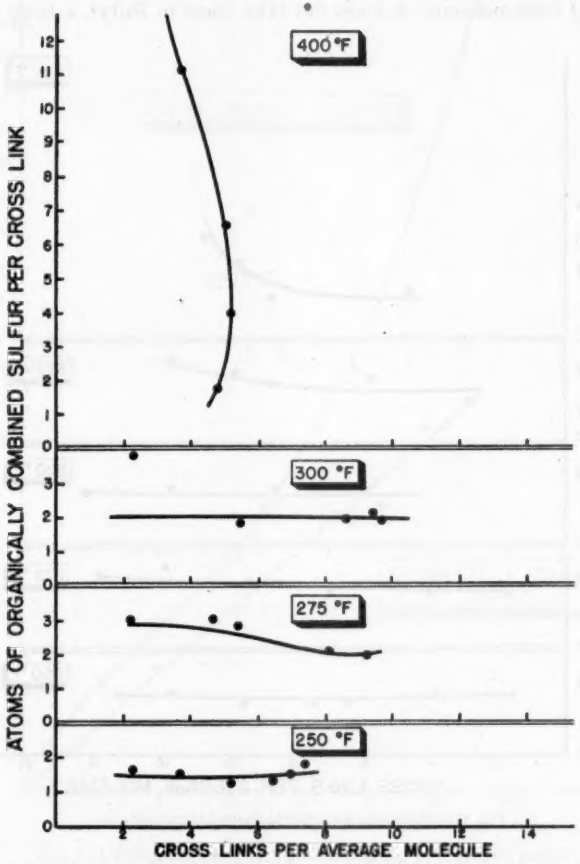


FIG. 10.—Tetramethylthiuram disulfide acceleration.

reversion has occurred. At higher curing temperatures, where reversion is evident, the amount of combined sulfur at the early stages of cross-linking also conforms to about two atoms of sulfur per cross-link. Thus it would appear that during the reversion process the lower-order sulfur linkages are broken instead of sulfur combining in large polysulfide bridges. In the vulcanization process hydrogen sulfide is usually formed through dehydrogenation of the

polymer, and the hydrogen sulfide so formed could decompose disulfide linkages in a manner analogous to the action of alkali metallic sulfides on dialkyl sulfides[18] with the formation of thiol groups attached to the polymer chain. In support of the last statement, experiments in these laboratories have shown that a Butyl vulcanizate can be degraded to a completely soluble state by heating in an atmosphere of hydrogen sulfide. In a polymer such as Butyl, where points of unsaturation are relatively far apart compared to natural rubber, the possibility of sulfur recombining in intramolecular form is quite remote. If intramolecular linkage did take place in Butyl, a large molecular

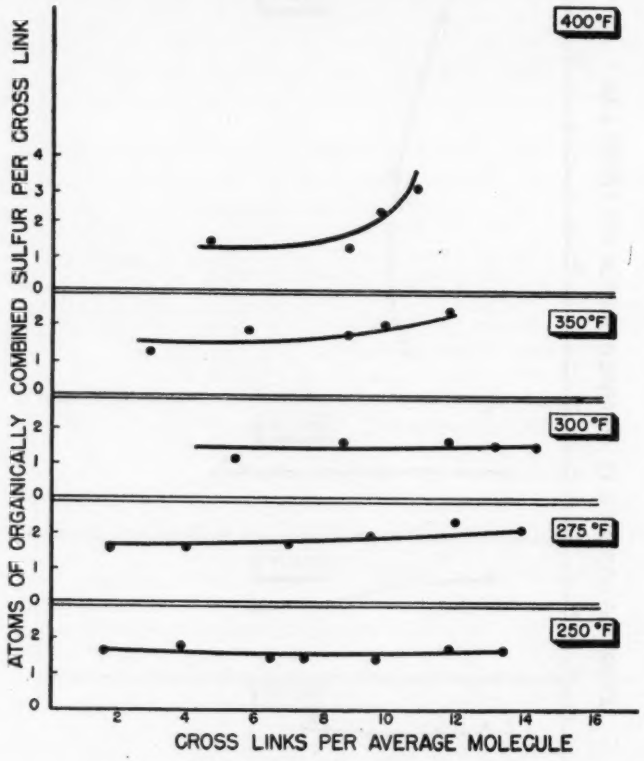


FIG. 11.—Tellurium diethyldithiocarbamate acceleration.

loop would result that would be capable of entangling in the network and thereby contribute something to the structure.

This stoichiometric study of sulfur vulcanization with a polymer of limited unsaturation has clarified, to some extent at least, the relation of combined sulfur to physical properties. It has often been stated[19] that the physical properties, for example elastic moduli, do not depend on the amount of combined sulfur. The data of Tables II and III for two different dithiocarbamate type accelerators have shown that the amount of combined sulfur per cross-link is essentially constant for different times and temperatures of vulcanization

until reversion occurs. Therefore, a direct relation between organically combined sulfur and physical properties can be made, for it has been shown that tension measurements are directly related to a cross-link index obtained from swelling measurements[5]. Figure 12 indicates in another manner how the proportion of combined sulfur is related to the concentration of cross-links. If total combined sulfur (that is, organically combined plus zinc sulfide sulfur)

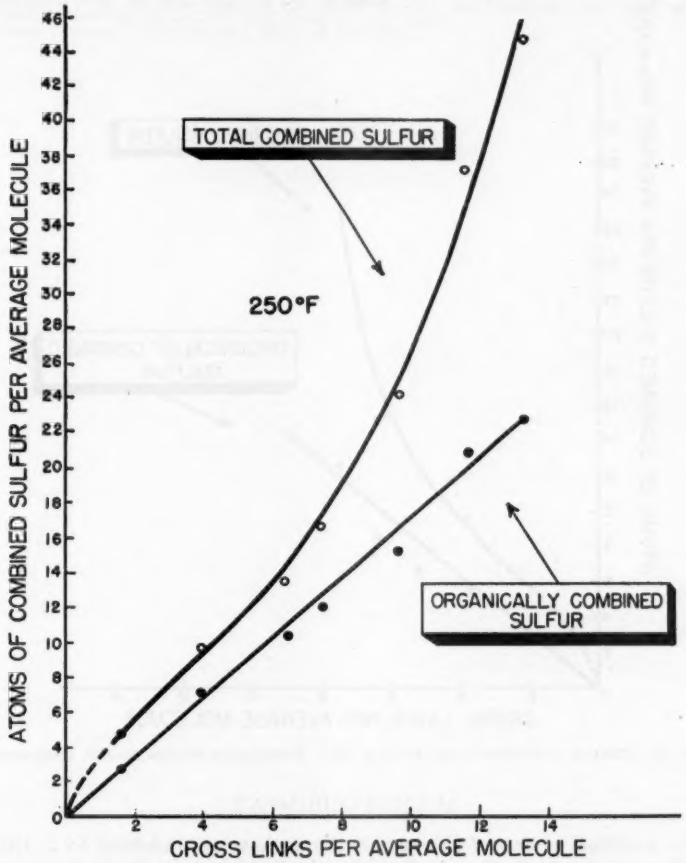


FIG. 12.—Relation of combined sulfur to cross links. Tellurium diethyl dithiocarbamate acceleration.

is related to cross-link concentration, an upward sweep is observed as the amount of sulfur in the form of zinc sulfide increases disproportionately. As is readily seen when only the organically combined sulfur is considered, a linear relation between cross-link concentration and the amount of sulfur exists. A similar illustration is given in Figure 13 with a TMTDS acceleration at 250° F. Although the points defining the relation between organically combined sulfur and cross-links are more scattered, a straight line through the origin, as in the

case of Figure 12, is the best fit. The slopes of the two lines are essentially the same as would be anticipated from the constancy of combined sulfur per cross-link shown in Tables II and III. Such linear relations are consistent with an orderly vulcanized network, and are definitely different from data reported for organically combined sulfur in natural rubber[20].

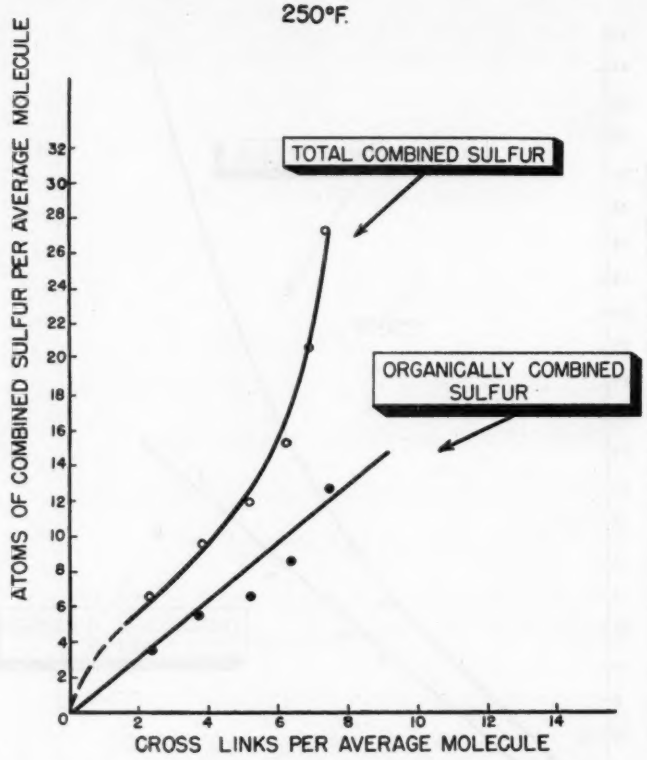


FIG. 13.—Relation of combined sulfur to cross links. Tetramethyl thiuram disulfide acceleration.

ACKNOWLEDGMENT

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ELASTIC MODULUS AND SWELLING OF BUTYL VULCANIZATES

INFLUENCE OF FILLERS *

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The reinforcement of rubberlike materials with fine particles has been the subject of considerable investigation, embracing attempts to obtain a criterion of reinforcement as well as to explain the nature of the rubber-particle bond. There have been many definitions of reinforcement, but in general most fine particles contribute toward an increase in the elastic rigidity of the rubber matrix. In addition to establishing criteria of reinforcement, an even more difficult problem is the study of the nature of the forces which contribute to elastic modulus.

It was recognized early that carbon black fillers possess unusual reinforcing properties when compared to mineral fillers as a class. Reinforcement by carbon particles was attributed to strong adsorptive forces[1] between rubber and filler, which immobilizes part of the rubber chain. Such a concept, which is akin to vulcanization, has also been proposed by other workers. For example, Naunton and Waring[2], on the basis of high frequency resilience effects, stated that carbon black sharply increases dynamic modulus with increased filler concentrations, whereas a fine zinc oxide pigment does not, and deduced that there is a more permanent bond between a carbon particle and rubber. Quantitatively the magnitude of this "strong" carbon-rubber bond has not been determined, but recent work[3] on the heats of adsorption of various hydrocarbon gases on carbon black indicates that this adsorption is essentially of the van der Waals type. However, initial heats of adsorption of 24 to 40 kg.-cal. per mole for C_{10} hydrocarbons[4] indicate very strong physical adsorption, which is consistent with the reinforcing behavior of carbon blacks. Recently, arguments have been presented[5] in favor of a chemical bond between rubber and the strongly reinforcing carbon blacks. It is somewhat difficult to distinguish between very strong physical and chemical adsorption. Barron[6] has shown that dilute solutions of rubber have a depressing action on the adsorption of other materials such as sulfur or stearic acid by carbon black, thus inferring a strong adsorption tendency between rubber and the carbon particle.

The first criterion of reinforcement was proposed by Wiegand[7], based on the enhancement of the tensile strength of rubber by certain carbon blacks.

Blake[8] criticized Wiegand's energy capacity theory on the basis of the proper cross-section. He claimed that no filler actually reinforced, because

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the tensile strength at break, based on the reduced cross-sectional area of the test-piece, did not increase when pigments were incorporated. Shepard[9] states Blake's criticism of the energy criterion is not valid, for the increase in energy of rupture (and tensile at break) due to pigmentation is accentuated when a correction is made for the reduced rubber content of a compound.

The criterion adopted for the present paper is based on the enhancement of the elastic modulus of rubber by the incorporation of pigments. More generally, it has been the purpose of the present paper to investigate in detail the effect of filler loading on the elastic properties of rubber networks by differentiating between volume and surface effects as functions of the concentration and the surface area of the filler. An added insight into the reinforcement phenomenon has been obtained through the study of the volume swelling of pigmented vulcanizates and the elastic properties of these swollen gels.

The present paper describes briefly the theoretical modulus-concentration relation pertaining to the volume effects caused by fillers in rubber. It points out that this relation is based on elasticity theory, that its analogy to the theoretical viscosity-concentration relation is useful in explaining some volume aspects of reinforcement, but that it is incomplete because it neglects the important surface-dependent effects caused by fillers. The paper also presents data on the equilibrium elastic properties of the rubber-pigment system and their interpretation. The equilibrium modulus is resolved into two additive components due to entropy and internal energy, respectively. The former is a volume consideration associated with the effect of filler volume upon the position and movement of the network molecules. The internal energy contribution is associated with the binding or restriction of the polymer chains by adsorptive forces. Data are also given on the elastic properties of swollen rubber-pigment systems and their interpretation. The rubber-carbon black bond is not broken by the swelling agent, whereas the rubber-mineral filler bond is broken.

THEORIES OF REINFORCEMENT

All fillers which wet the rubber matrix increase its elastic modulus with increasing concentration. The observed increase of the modulus can be compared with the increase predicted for an idealized rubber-filler system of the following properties:

The filler particles are rigid spheres; they do not need to be equal in size.

Complete wetting of filler by the rubber is assumed. This assumption implies that the rubber-filler bond is not localized, but can slide on the surface of the filler.

Hooke's law holds for both the rubber matrix and the rubber-filler system. This assumption implies that the viscoelastic properties of the rubber matrix and of the rubber-filler system are negligible. Consequently, the theory should be compared with "equilibrium" stress-strain data.

Elastic interaction is assumed to operate for more concentrated rubber-filler systems. Only the interaction of pairs of particles is taken into account, that of three or more particles being neglected.

Application of elasticity theory then leads to the relation[10]:

$$E = E_0(1 + 2.5c + 14.1c^2) \tag{1}$$

where E is Young's modulus for the matrix-filler system, E_0 is that for the matrix alone, and c is the volume concentration. Thus the ratio E/E_0 de-

pends only on the concentration. Equation 1 is here called the "theoretical modulus-concentration relation".

The first two terms of Equation 1 are the same as those in Einstein's well known law of the viscosity of spherical suspensions:

$$\eta = \eta_0(1 + 2.5c) \tag{2}$$

For more concentrated suspensions, Equation 2 was extended by Guth and Gold[11] to:

$$\eta = \eta_0(1 + 2.5c + 14.1c^2) \tag{3}$$

the third term in the bracket being identical with the corresponding term in Equation 1; η and η_0 are the viscosities of the suspension and the solvent, respectively.

Equations 2 and 3 were obtained from the hydrodynamics of viscous liquids. The suspended particles perturb the flow in a viscometer, and this perturbation increases the energy dissipated, which is reflected in an increase in the viscosity of the solvent.

The assumptions needed to derive Equation 3 are analogous to the assumptions listed above; Hooke's law of elasticity is replaced by Newton's law of viscosity and "elastic interaction" is replaced by its "hydrodynamics" counterpart.

Equation 1 holds strictly only for Young's modulus, *i.e.*, the slope of the stress-strain curve at the origin. It is valid, however, more generally for other points on the stress-strain curve, as long as the stress-strain curve for the loaded stock is similar to that of the gum stock, *i.e.*, as long as they differ only by a multiplicative factor. For 50 per cent extension, used in this study, this condition can be expected to hold with fair accuracy, inasmuch as for a loaded GR-S compound the similarity was shown to hold up to 100 per cent extension[12]. Thus Equation 1 may be written in the form:

$$M = M_0(1 + 2.5c + 14.1c^2) \tag{4}$$

where M is the elastic or equilibrium modulus at 50 per cent extension of the loaded rubber, and M_0 is the elastic modulus of the unpigmented compound.

In the case of viscosity of suspensions, deviations from Equation 2 can be explained on the basis of solvation at the particle surface, which is a binding of the particle with a liquid layer. Another deviation from the viscosity equation, especially at higher concentrations of filler, arises when there is a formation of particle network structures. Similarly, deviations from Equation 3 for rubber-pigment systems may be caused by binding and filler network formation. Higher concentrations of carbon black increase the changes of particle interaction, and thus cause a more rapid rise in elastic modulus than is predicted by Equation 3. Some types of blacks accentuate this effect because they are known to possess a persistent reticulate structure[13]. The effect of particle chains can be approximated quantitatively by considering rodlike particles embedded in the rubber. For such particles an equation similar in form to Equation 1 is obtained[10]:

$$M = M_0(1 + 0.62fc + 1.62f^2c^2) \tag{5}$$

where f is the shape factor (length-diameter). By estimating the shape factor of reticulate carbon chains from electron microscope pictures, Cohan and Smith[14] have approximated experimental stress data with Equation 5. They

used extension modulus and arbitrary Shore hardness values converted to compression modulus.

There are some aspects of reinforcement, however, that cannot be adequately explained by the theoretical modulus-concentration relation. For example, the increase in stiffness and bound rubber values with time is a common observation, and indicates the occurrence of slow adsorption of rubber on the active pigment particle. Also, the volume concentration concept predicts that reinforcement is independent of particle size of the filler, and tends to account for any deviation by a shape factor[14]. Although the shape factor undoubtedly influences reinforcing effects, asymmetry of the particle is not necessary for reinforcement. Indeed, some extremely asymmetric particles like diatomaceous earth do possess a stiffening effect, but their contribution to the elastic or equilibrium modulus is relatively small. Clay pigments also fall into this category.

Weiss[15] has resolved the free energy of reinforcement into surface energy and elastic energy components:

$$F = Fs + Fe \tag{6}$$

Total free surface energy, Fs, would depend on the total surface area of the filler particles, while the total free elastic energy depends on the volume concentration. Previous to the development of Equations 1 and 5, Rehner[16] set up expressions for the stresses about a spherical particle embedded in an elastic material under uniform tension. He showed that the average radial stress is independent of particle size but depends on filler concentration and the elastic constants of the materials under consideration. This resolution of the energy of reinforcement into surface energy and elastic energy components is a step toward a further understanding of the reinforcement phenomenon. That there is some surface effect that contributes to the unusual behavior of carbon blacks is universally recognized, and the data given below confirm the existence of a carbon black surface contribution to reinforcement.

ELASTIC PROPERTIES OF POLYMER–PIGMENT SYSTEMS

In studying the reinforcement of polymer networks by pigments, it is necessary to utilize various systems having the same concentration of chemical cross-links. One method of closely approaching such a condition is to use a polymer of limited unsaturation, which markedly reduces the probability of intramolecular linkages, and to incorporate an excess of sulfur and accelerator over that required to yield a maximum state of vulcanization (concentration of cross-links). It has been demonstrated with a polymer such as Butyl rubber that a maximum state of vulcanization can be obtained where further additions of sulfur and accelerator do not increase the cross-linking[17]. With an excess of curing agents, differences in the adsorptive capacities of the added pigments do not alter the concentration of chemical cross-links. In a system where the polymeric unsaturation is far in excess of the curative agents that promote vulcanization (as in vulcanizates of natural rubber or other diene-type polymers) differences in the adsorptive capacity of the added fillers may result in changes in the concentration of chemical cross-links of the final vulcanizates by removing some of the curatives from the field of reaction.

In the present study, a Butyl rubber of commercial GR-I grade was used. An unpigmented master batch of polymer, zinc oxide, and sulfur was first prepared. To aliquot portions of this mixture were added 5, 10, 20, 30, 40, and

50 volumes of various fillers per 100 volumes of polymer in the master batch. The accelerator, tellurium diethyldithiocarbamate, was added in a ratio of 1.5 parts to 100 parts of GR-I after the filler had been incorporated, to avoid precuring during compounding. The formula was as follows:

GR-I	100
Zinc oxide	5
Sulfur	2
Tellurium diethyldithiocarbamate	1.5
Filler	Varied

The pigments used included various grades of carbon black and some mineral fillers:

Pigment	Particle size[18] mμ
High abrasion furnace black (HAF)	32
Fine furnace black (FF)	34
Semireinforcing furnace black (SRF)	81
Medium thermal black (MT)	274
Precipitated calcium silicate	40–50
Precipitated calcium carbonate	87
"Soft" clay	—

The compounds were cured at 300° F for 80 minutes; this ensured reaching the flattened or level portion of the GR-I vulcanization curve[17]. Test samples were cut from 2 × 2.5 × 0.035 inch slabs.

Equilibrium modulus.—Equilibrium moduli were determined with a triple beam balance[19] attached to a calibrated glass float[20] that facilitates rapid change in load to compensate for the relaxation of stress in the extended sample. Stresses were determined at 50 per cent elongation at temperatures ranging from 150° to 0° F. The sample was first relaxed at 150° F, the temperature was then lowered gradually, and the change in stress was noted with the hydrostatic balance. The extension of the sample was adjusted with the aid of a cathetometer focused on pieces of very thin wire which pierced the sample at a separation of 1 cm. in the unstretched specimen. The exact unstretched distances were measured with a measuring microscope; these distances were then extended 50 per cent on the triple-beam apparatus and checked throughout the experiment.

Straight lines were obtained on plotting stress *vs.* temperature, in accordance with the theory of Guth and James[21], who have related stress to absolute temperature according to the equation:

$$Z = KT\left(1 + e - \frac{1}{(1+e)^2}\right) \tag{7}$$

$$e = \frac{l - l_0}{l_0}$$

where Z = stress, T = absolute temperature, K = constant, and l and l_0 are extended and original length.

Two representative series of curves are shown in Figures 1 and 2. Figure 1 is a series of curves showing the effect of loading on the temperature-stress relationship when a relatively large medium thermal carbon black is used. Both the slope and the overall stress increase with increased loading of pigment. In Figure 2 a high reinforcing furnace black of finer particle size exhibits a different pattern as loading is increased. The total stress increases with loading, but as

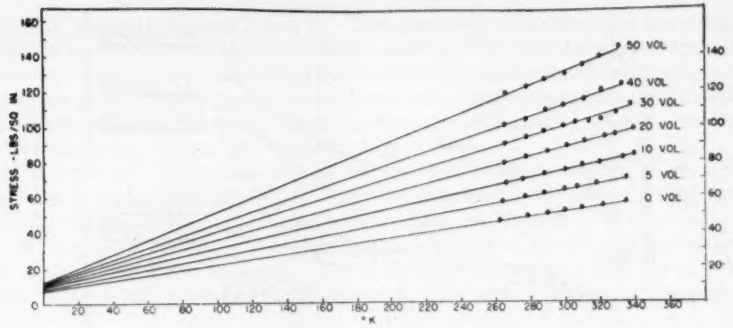

FIG. 1.—Equilibrium stress at 50% elongation as function of temperature. Medium thermal carbon, 274 mμ.

the concentration of filler is increased to 40 and 50 volumes the slope of the lines decreases. This indicates that the high surface forces and the structural effects of the carbon chains have interfered with the thermal elastic properties of the rubber matrix.

Mineral fillers such as precipitated calcium carbonate behave similarly to the medium thermal carbon black with respect to the effect of loading on the temperature-stress functions. Other mineral fillers, such as clays, that possess

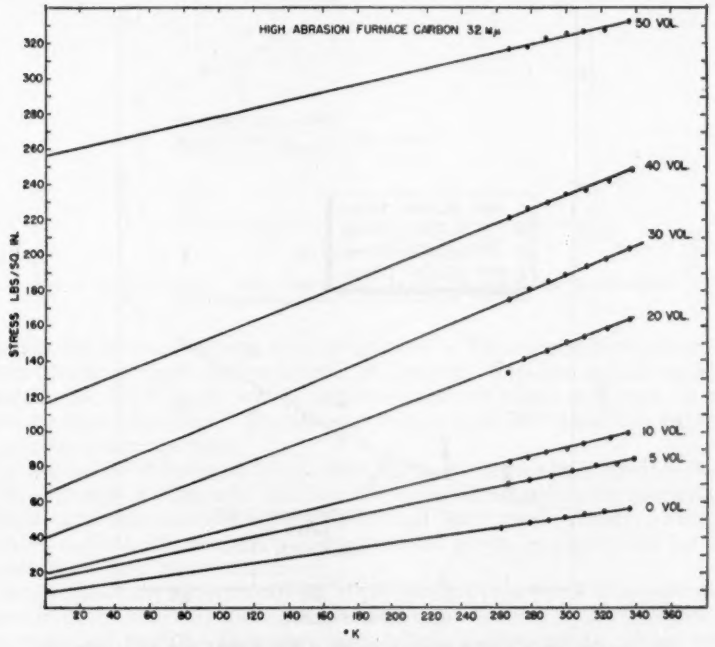

FIG. 2.—Equilibrium stress as function of temperature. 50% elongation.

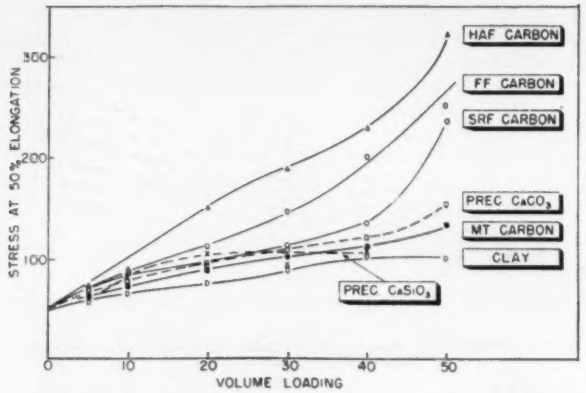

FIG. 3.—Equilibrium modulus as function of filler loading. 25° C temperature.

asymmetric habits exhibit a sudden inability to contribute to the stress of a network as loading is increased. The same effect has been observed for precipitated calcium silicate of very fine particle size. This type of behavior is shown in Figure 3, where equilibrium stress at 25° C (298° K) is plotted as a function of filler loading. The stress values were obtained from a series of straight lines

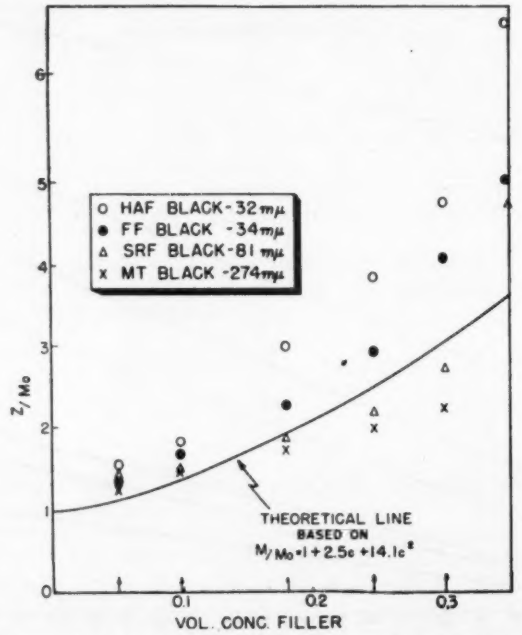

FIG. 4.—Comparison of total stress as function of filler concentration with theoretical modulus concentration relation. Carbon black.

similar to those of Figures 1 and 2. The curves for the clay and the silicate pigments level off, while the other fillers continue to contribute to stress with increased loading. On this basis, there is wide divergence in the reinforcement that these various fillers impart to an elastic stress, and some of them obviously do not conform with the theory based on the viscosity analog, wherein increase in stress depends only on the concentration of filler.

If the data of Figure 3 are plotted on the basis of stress relative to that obtained for an unloaded vulcanizate, a great divergence in the effect of filler concentration is still noted. In Figure 4 the ordinate is plotted as Z/M_0, where Z and M_0 are, respectively, the equilibrium stress of the loaded compound and that of the unloaded compound. The abscissa is the volume fraction of filler based on the total volume of the compounded material. The solid line repre-

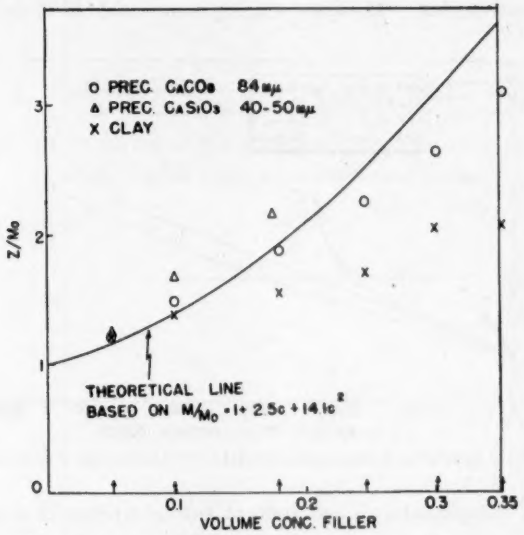

FIG. 5.—Mineral fillers. Comparison of total stress as function of filler concentration with theoretical modulus concentration relation.

sents the theoretical viscosity analog equation[3]. The experimental points for carbon blacks in Figure 4 diverge from the theory. The fine particle carbons, especially the HAF black, which possesses some reticulate structure, lie well above the theoretical line. The coarsest particle size, MT black, falls below at higher filler concentrations.

In the case of the mineral fillers, there is less divergence from the theoretical curve, as shown in Figure 5. In fact, the experimental points for precipitated calcium carbonate conform to the theoretical curve fairly closely. For precipitated calcium silicate, the few experimental points lie above, and for clay the points are well below, the curve.

As discussed above, explanations of the upward divergence of experimental values from the viscosity analog are based on a departure of the filler particle from spherical habit[22]. However, clay, which is asymmetric, yields stress values that fall below, indicating that surface forces must be a factor in the rein-

forcement phenomenon. In the case of the carbon blacks of Figure 4, FF black has an essentially spherical habit, but its stress values lie consistently above the theoretical curve. Yet the explanation of stress reinforcement cannot be based solely on the extent of the surface exposed to the rubber matrix. In Figure 9 this is graphically shown in a plot of Z/M_0 against extent of surface instead of volume concentration of filler. Each carbon type exhibits its own stress-surface curve, and the finer particle surface appears less effective in reinforcing stress. In other words, increase in the elastic modulus cannot be solely a function of particle size or surface area of the incorporated filler. Therefore, to gain further insight into the filler effect, reinforcement must be considered in terms of components of total stress.

Components of stress.—Anthony, Caston, and Guth[23] have shown that stress in a stretched sample of rubber consists of an internal energy contribution and an entropy contribution. These are roughly comparable to Weiss' surface and

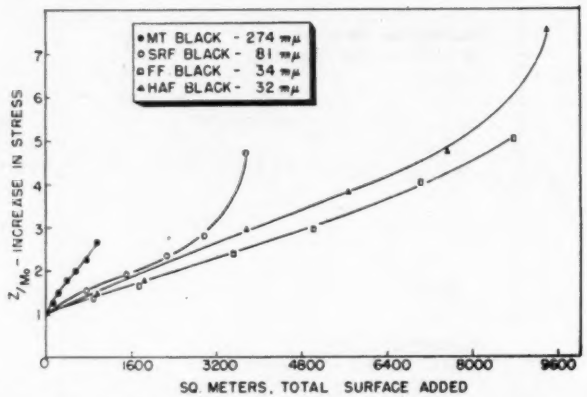

FIG. 6.—Increase in equilibrium modulus over unloaded control as function of total surface added.

elastic energy components. Their concept can be written in equation form:

$$Z = Z_u + Z_s \tag{8}$$

where Z = total stress, Z_u = stress due to internal energy, and Z_s = entropy contribution.

Z_u is actually the stress component due to enthalpy[24]:

$$\left(\frac{\partial Z}{\partial T}\right)_{L.V.} \text{ being } \left(\frac{\partial Z}{\partial T}\right)_{L}$$

but because the difference between enthalpy and internal energy is small, the notation Z_u is more suggestive.

In an unloaded network the contribution of internal energy to stress is small, so total stress at a given temperature and elongation depends to a large extent on entropy, *i.e.*, the movement and position of the chain segments in the network. When fillers are incorporated into a vulcanized rubber, the relative entropy and internal energy contributions to stress are changed. The series of straight lines shown in Figures 1 and 2 offer a method of graphically obtain-

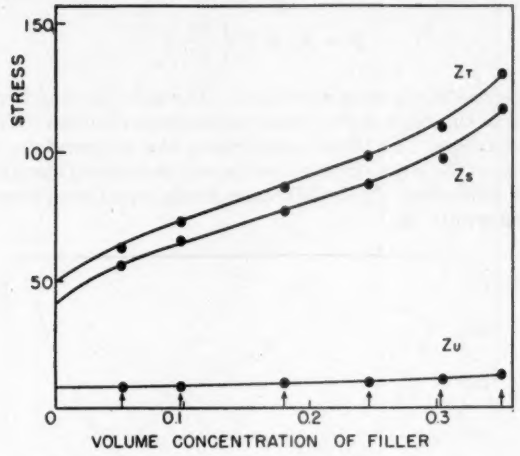

FIG. 7.—Medium thermal carbon contributions to stress.

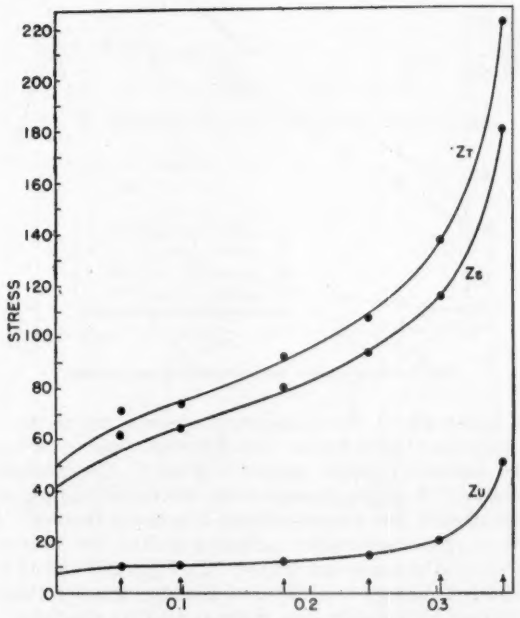

FIG. 8.—Semireinforcing carbon contributions to stress.

ing the two components of stress. Equation 8 can be written in the form:

$$Z = Z_u + T\left(\frac{\partial Z}{\partial T}\right)_L \tag{9}$$

which defines stress at constant extension. The entropy contribution can then be obtained from the slope of the stress temperature function multiplied by the absolute temperature. In these comparisons the temperature of 298° K or 25° C was used. The total stress is known, so the internal energy contribution is obtained by difference. This difference should equal the extrapolated intercepts of the lines at 0° K.

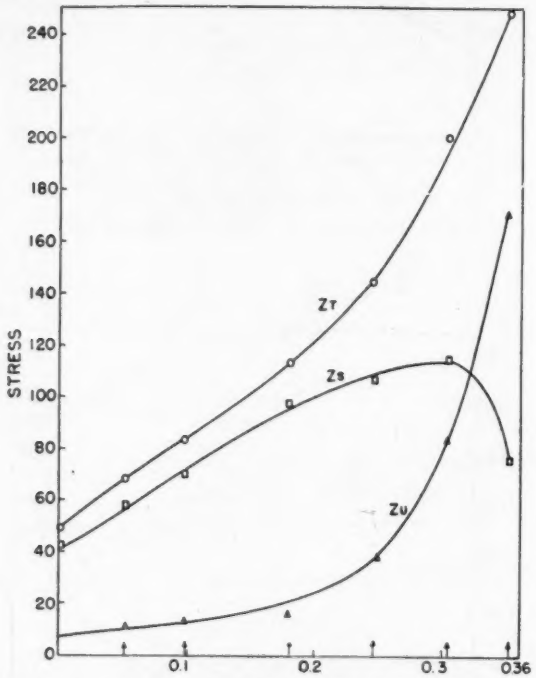

FIG. 9.—Fine furnace carbon contributions to stress.

In Figures 7 through 10, the components of stress are plotted as a function of the volume fraction of filler for the four different types of carbon blacks. In the case of the medium thermal carbon (Figure 7), the internal energy contribution shows only a slight increase with increased loading of filler. The increase in total stress is due almost entirely to entropy factors. As the carbon blacks increase in surface area and reinforcing ability, the internal energy contribution asserts itself to a marked degree. In Figures 9 and 10 at higher filler loadings the internal energy contribution becomes greater than the entropy contribution, indicating a loss in long range rubberlike elasticity.

The theories of reinforcement, already referred to, emphasize the elastic contribution to stress and predict that the stress reinforcement is independent

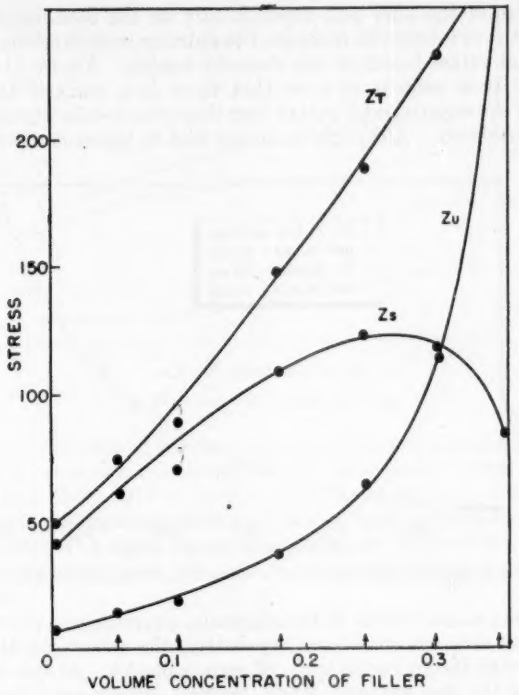

FIG. 10.—High abrasion furnace carbon contributions to stress.

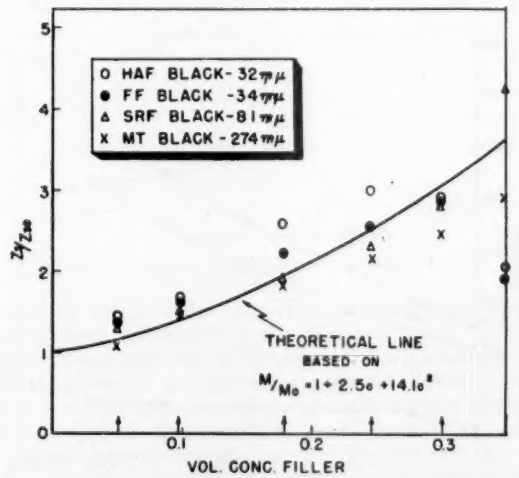

FIG. 11.—Comparison of entropy contribution of stress as function of filler concentration with theoretical modulus concentration relation. Carbon black.

of particle size of the filler and depends only on the concentration. In this connection, it is of interest to compare the entropy contributions of stress with the theoretical values based on the viscosity analog. Figure 11 shows such a comparison. It is evident at once that there is a marked decrease in the divergence of the experimental points over that observed in Figure 4 when total stress was considered. Although we do not wish to ignore completely consider-

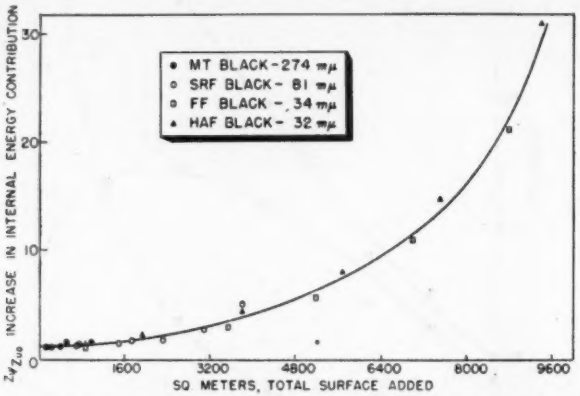

FIG. 12.—Increase in internal energy contribution as function of total surface of carbon black added.

ations involving shape factors of the pigments, nevertheless, when the entropy contribution of stress is considered separately, the experimental points agree more closely with theory for all types of carbon blacks. At the very high concentrations of the fine carbons, where internal energy contributions rise inordinately high and entropy contributions decrease with increasing concentration, this superior correlation breaks down.

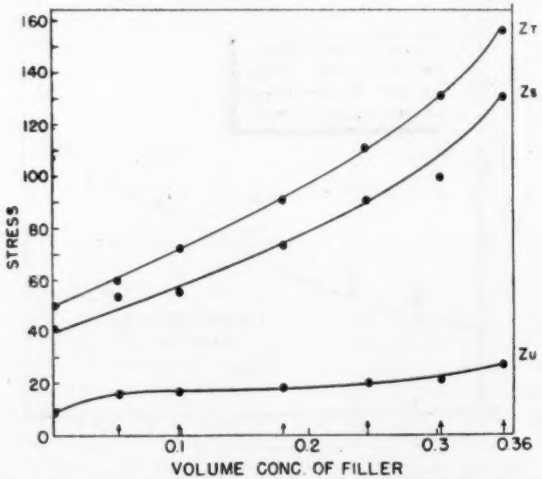

FIG. 13.—Precipitated calcium carbonate contributions to stress.

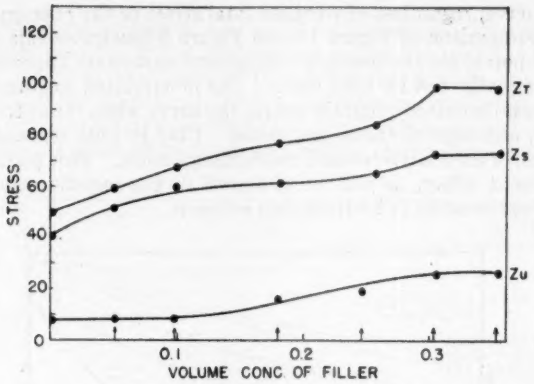

FIG. 14.—Clay contributions to stress.

Resolution of the data of Figure 6 into their stress components has revealed that the internal energy contribution can be more readily correlated with the total surface area of the carbon black present in the rubber. Figure 12 shows that the internal energy contribution of four different grades of carbon black can be represented as a single continuous fuction of total surface area of black added. The increase in total stress did not behave in this manner for the four types of blacks.

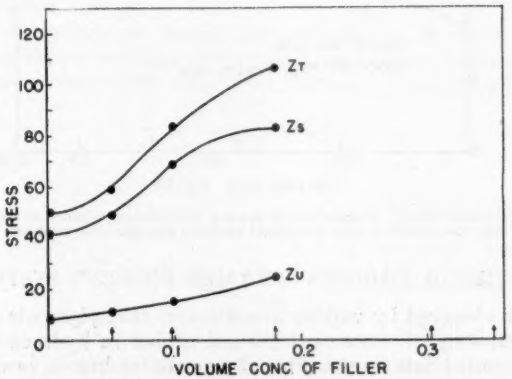

FIG. 15.—Precipitated calcium silicate contributions to stress.

Mineral fillers do not give the large internal energy contribution to stress observed with the carbon blacks (Figures 13 through 15). The entropy contribution to stress is predominant at all concentrations of filler. Only the precipitated calcium carbonate is able to maintain an elastic structure up to a volume fraction concentration of 0.35; clay and calcium silicate eventually yield polymer filler systems that exhibit excessive permanent set at low elongations as filler concentration is raised.

Because the entropy contribution to stress predominates in the case of mineral fillers, there is little difference in the correlation of stress data with the

theoretical curves, regardless of whether total stress or the entropy component is used. A comparison of Figure 16 and Figure 5 illustrates this point. The experimental points for the precipitated calcium carbonate approach the theoretical curve equally well for both cases. For precipitated calcium silicate, the few experimental points are slightly nearer the curve when the entropy function is considered, although the data are sparse. Clay in both instances falls well below, because of its relatively small reinforcing action. This pigment imparts mainly a diluent effect, as will be observed in the experiments on volume swelling of these systems in hydrocarbon solvents.

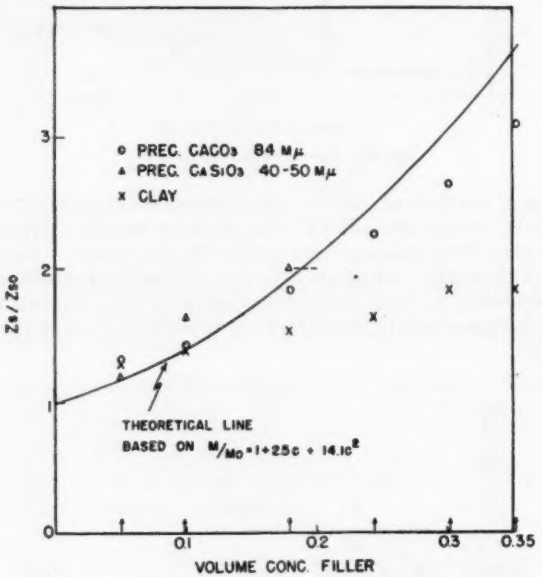

FIG. 16.—Mineral fillers. Comparison of entropy contribution of stress as function of filler concentration with theoretical modulus concentration relation.

PROPERTIES OF SWOLLEN POLYMER PIGMENT SYSTEMS

It has been observed by various investigators that pigments or fillers alter the swelling capacity of vulcanized natural rubber in hydrocarbon solvents. Scott[25] has presented data on the effect of pigment loading on swelling capacity and has shown that carbon blacks restrict swelling to a much greater extent than do mineral pigments. Indeed, some mineral fillers such as barytes increase the swelling capacity of a vulcanized natural rubber as loading is increased[26]. Such behavior would indicate a complete lack of any polymer-pigment bonding. Parallel observations have been made with Butyl rubber-pigment systems when the networks are swollen in a hydrocarbon solvent.

Restriction of volume swelling.—Volume swelling experiments were carried out in cyclohexane at 25° C. Equilibrium was established in about 24 hours, and the amount of swelling was determined from the weight of cyclohexane imbibed. The swelling capacity was expressed as percentage volume increase, based on the polymer content of the pigment-rubber mixture. Figure 17 shows

some results with the various fillers. It is evident at once that carbon blacks exhibit a greater capacity to restrict volume swelling than do the mineral fillers. In addition, the finer the particle diameter the greater is this restriction. Mineral fillers, on the other hand, impart only a limited restriction to the swelling capacity as the volume concentration of filler is increased. Calcium silicate initially yields the greatest decrease in swelling, but is finally surpassed by

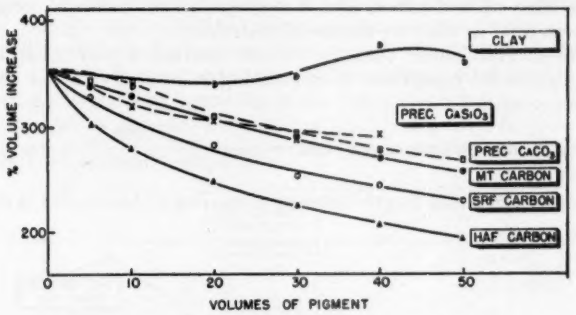

FIG. 17.—Restriction in swelling capacity by filler loadings.

precipitated calcium carbonate. "Soft" clay exhibits a negative effect as the filler loading increases, in agreement with some observations made in natural rubber compounds[25].

Volume swelling-pigment loading curves serve to illustrate a feature of carbon black reinforcement that is novel and certainly indicates a type of surface energy not possessed by other filler surfaces. It will be recalled from

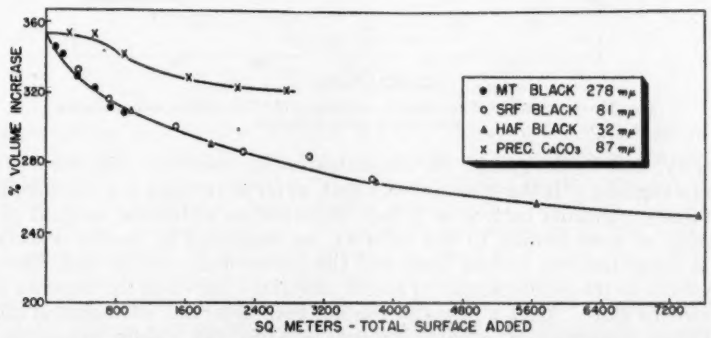

FIG. 18.—Restriction of swelling as function of total surface area added.

Figure 6 that the elastic modulus imparted to a vulcanizate did not depend solely on the surface area of the incorporated carbon black. However, in the cases of restriction of volume swelling there appears to be a direct correlation with the extent of the carbon black surface. In Figure 18 the swelling capacity is shown as a function of the total pigment surface area for the three types of carbon black. In this relationship a correction is made for the volume occupied

by the filler in the swollen matrix, and this correction is added to the percentage volume increase based on the amount of solvent imbibed by the rubber hydrocarbon. For example, if the volume increase due to solvent imbibition is 300 per cent based on polymer content, then the corrected swelling would be 300 per cent plus the volume of filler per 100 volumes of polymer. The experimental points for the three types of carbon black fall on a single line. A similar analysis was made for calcium carbonate with a particle size about equal to that of the SRF carbon black, and it is evident that different magnitudes of surface forces exist in the two classes of materials.

It has been established[27] that the volume fraction of polymer in the swollen gel in nonpigmented compound is related logarithmically to the chain length between the cross-links.

$$\text{Volume fraction of polymer} = \frac{100}{\%\text{ volume increase} + 100}$$

The shorter the chain length between cross-links, the smaller is the swelling

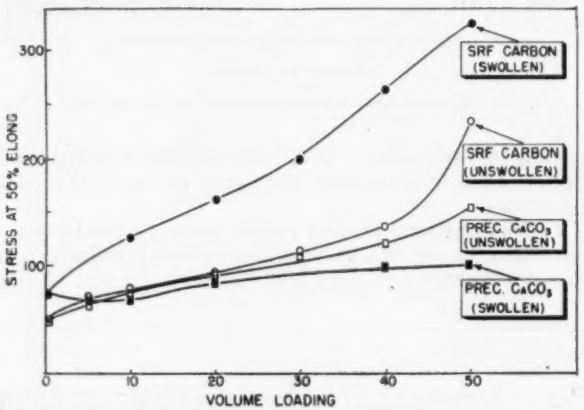

FIG. 19.—Comparison of equilibrium modulus at 25° C of swollen and unswollen networks at same extension.

capacity, that is, the greater the concentration of cross-links, the lower is the volume swelling. It therefore appears that, as far as swelling is concerned, true reinforcing pigments behave as if they imparted an additional amount of restriction or cross-linking to the network, as suggested by earlier workers[28]. These forces between carbon black and the rubber chain enable such fillers to contribute to the reinforcement of elastic modulus even when the network is in the swollen state. Such a behavior has not been observed with mineral fillers.

Elastic properties of swollen networks.—When the elastic properties of swollen and unswollen networks containing fillers were compared, an entirely different behavior between carbon blacks and mineral fillers was observed. The elastic modulus of the swollen networks was determined at 50 per cent extension while the test-specimen was immersed in cyclohexane. In testing the swollen specimen, no period of time at elevated temperatures was needed to relax the sample to a state of equilibrium; swollen specimens respond rapidly to changing stress. Therefore the elastic modulus was determined directly at 25° C.

To compare the carbon and mineral filler surfaces, two pigments of similar average particle diameter were selected: SRF carbon black 81 mμ, and a precipitated calcium carbonate of 87 mμ. In Figure 19 elastic moduli of the swollen and unswollen specimens at 50 per cent elongation are compared as a function of filler concentration. It is evident that the carbon black shows an opposite trend to the calcium carbonate. In the case of carbon black, the elastic modulus is markedly higher for the swollen system; for calcium carbonate, the opposite is true. This decrease in elastic modulus on swelling in the later case exists, even though the individual polymer chains are actually in a state of higher extension, due to the fact that the solvent has distended the network. With carbon black it is apparent that the higher elastic modulus of the swollen network reflects this added extension of the polymer chains.

It is reasonable to assume, from such a model of a cross-linked network as the tetrahedron of Flory and Rehner[28], that the average linear extension of the

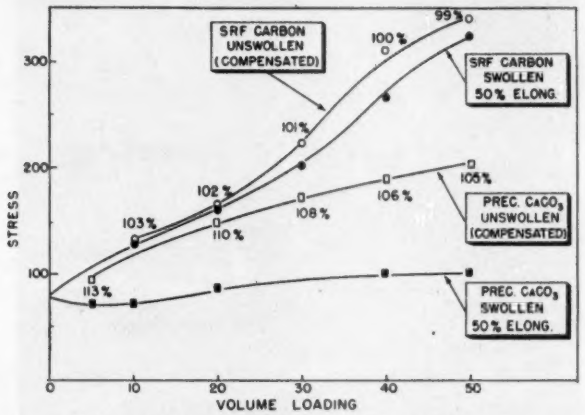

FIG. 20.—Comparison of swollen equilibrium modulus at 50% extension with unswollen specimens of compensated extension.

polymer chains in a swollen network is proportional to the cube root of the volume increase. Therefore, if the reinforcing bond persists in the swollen state, the swollen elastic modulus should be equivalent to an unswollen elastic modulus at an additional compensating elongation. Based on the volume swelling of the various loadings, compensating elongations in the unswollen state were calculated so that the reinforcing effect in swollen and unswollen specimens could be compared at the same average extension of the individual chains. (In a swollen sample the average internal extension of the individual molecular chains is considered to be the cube root of the volume expansion. Therefore, in comparing stresses at similar extensions of the molecular chains, unswollen samples must be given an additional external stretch to compensate for the extension due to swelling.) Stresses at compensated elongations are shown at the appropriate points on the curves for the unswollen samples in Figure 20. These curves compare the elastic moduli of swollen specimens at 50 per cent extension with the elastic moduli of unswollen specimens at a compensating elongation, as a function of filler loading. For SRF carbon black, the compensated unswollen elastic moduli and the swollen moduli at 50 percent

extension are comparable. The shape or curvature of the functions is similar. For the precipitated calcium carbonate, the compensated unswollen moduli are far higher than the comparable swollen moduli. The divergence is greater than that observed in the previous figure, where all comparisons are made at the same external extension.

These results serve to illustrate graphically the role of the carbon black surface in reinforcing rubberlike polymer. The carbon black bond is sufficiently strong to persist even while the network is in the swollen state, while the weak surface bonds of the mineral fillers are broken by the spreading action of the imbibed solvent.

FIG. 21.—Clay in extended Butyl vulcanizate (× 970). Showing voids about individual particles. 5 volumes of clay to 100 volumes of GR-I. 350% elongation.

SUMMARY

The reinforcing of elastomeric vulcanizates by filler particles has been studied with Butyl rubber, a polymer of limited unsaturation. This limited unsaturation enables a comparison to be made of filler reinforcement in materials having a constant concentration of chemical cross-links, because excess curing agents can be added without increasing the state of cure byond a certain limit. Under such conditions differences in the adsorptive powers of fillers do not result in variations in the ultimate state of vulcanization.

Reinforcement in this paper was defined as the ability of a pigment to enhance the elastic or equilibrium stress (at constant elongation) of a vulcanized specimen. Equilibrium stress at 50 per cent elongation was determined on a

triple-beam balance, and the internal energy and entropy components of stress were determined. The entropy component of stress was found to conform more closely to the classical viscosity analog equation for reinforcement, where only the volume concentration of filler and not the surface area is the controlling factor. It was observed that carbon blacks, especially those of finer particle size, produced a greater internal energy contribution to stress than did mineral fillers, which appeared as a function of the total pigment surface added. The increase in stress observed with mineral fillers was due largely to entropy contributions.

Another manifestation of reinforcement was shown to be the restriction of volume swelling of a network (in a good solvent) in the presence of pigments. Carbon blacks showed the greatest restriction of swelling capacity, and in distinction to stress behavior, this restriction was solely a function of the total surface area of carbon black present, regardless of type. With mineral fillers, far less restriction was observed, and in one case an increase in swelling was noted. This can be attributed to poor bonding, which results in voids. The photomicrograph of clay particles in a thin stretched section of Butyl shows this effect in Figure 21. The role of surface forces in the case of carbon blacks has been further demonstrated through measurements of the elastic properties of swollen rubber. The reinforcing nature of carbon black is maintained in a swollen network, while the weak bonds between the polymer and a mineral filler are destroyed when the chains are separated by the imbibed solvent, and the stress then approaches that of an unloaded compound.

ACKNOWLEDGMENT

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THE TRANSFORMATION OF THIOLS COMPOUNDED IN RAW RUBBER *

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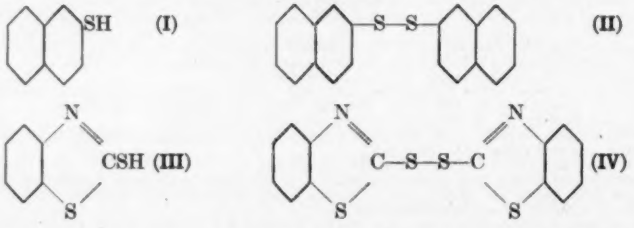
During the last few years the rubber industry has made use of certain thiols, under the technical name of peptizing agents, which have the property of accelerating the plasticization of raw rubber during mastication. It is now known that this process of plasticization involves oxidation of the rubber[1], and that it does not take place in an atmosphere of an inert gas[2].

Accordingly the present authors were induced, on the one hand, to follow the transformation of thiols during their participation in the mastication of rubber and, on the other hand, to observe their influence on the tendency of rubber to oxidize.

In the first of these objectives, the analytical method utilized was ultraviolet absorption spectrography[3]. To avoid pertubations in the spectra caused by the resins present in rubber, crepe rubber purified by acetone extraction was used in the experiments. The rubber was masticated at 100° C, and the thiol was added soon after the beginning of this mastication in the proportion of 5 per cent of the rubber. Samples were withdrawn at successive intervals of time, and the transformation products of the thiol, which were isolated by acetone extraction, were identified by their ultraviolet absorption spectra. In these experiments, chloroform solutions containing 0.5 gram per liter were employed.

These absorption spectra change with the time of mastication. In the case of 2-naphthalenethiol (I), the Hartley line, which is represented by the continuous curve in Figure 1, changes progressively and assumes the form indicated by the broken curve in Figure 1, which corresponds to the absorption spectrum of 2-napthyl disulfide (II). Similarly, mercaptobenzothiazole (III) gives benzothiazolyl disulfide (IV), as shown in Figure 2. This confirms the results obtained by Twiss[4], obtained by chemical analysis.



In the present work it was proved that the transformation of 2-naphthalenethiol into 2-naphthyl disulfide is much more rapid than the transformation of mercaptobenzothiazole into benzothiazolyl disulfide, and this is in accord with

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 232, No. 1, pages 82–84, January 5, 1951.

the intensity of the plasticizing effects of these two thiols, *e.g.*, 2-naphthalenethiol has a definitely greater plasticizing action than has mercaptobenzothiazole.

Additional experiments have shown that the presence of even very small amounts of sulfur inhibit completely the plasticizing action of thiols, and the spectrum confirms the fact that, under these conditions, mercaptobenzothiazole is no longer transformed into benzothiazolyl disulfide[5].

To determine the influence of thiols on the tendency of rubber to oxidize, thiols were added to rubber during mild mastication at ordinary temperature[6], and the oxidizability was measured at 80° C by the manometric method[7]. Figure 3 shows the results obtained.

In the presence of 2-naphthalenethiol, the oxidation was at first very rapid, and the higher the percentage of 2-naphthalenethiol originally, the more rapid was the oxidation. The rate of oxidation then decreased and became virtually the same as that of a control sample containing no thiol. With mercaptobenzothiazole, the transition between the two phases of oxidation was much more gradual and less well defined, as is evident by the broken curves in Figure 3. This is explained by the fact that the transformation of mercaptobenzothiazole into benzothiazolyl disulfide is much slower than the transformation of 2-naphthalenethiol into 2-naphthyl disulfide.

These two series of experiments explain the mechanism of the action of so-called peptizing agents. A thiol acts, in effect as a prooxygenic agent and thereby promotes plasticization. However, because of the phenomenon recognized as exhaustion of a catalyst, the thiol is transformed, little by little, by secondary oxidation into the corresponding disulfide. The oxidation curves show that mercaptobenzothiazole withstands this tendency toward exhaustion longer than does 2-naphthalenethiol.

It is of interest in this connection to call attention to the similarity of structure between these products and deactivating agents[8]. If one studies, for example, the aging of a vulcanizate prepared from rubber plasticized by means of 2-naphthalenethiol, it will be found that the aging is better than that of a control vulcanizate prepared from rubber plasticized by simple milling. Likewise the action of an antioxygenic agent is increased.

From the technical viewpoint, therefore, these thiols have a dual favorable effect; first, they act as accelerators of oxidation during mastication and, secondly, their transformation products, by functioning as deactivating agents, contribute toward good aging after vulcanization.

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BUTADIENE AND ITS POLYMERS. V. FORMATION OF SPONGY BUTADIENE POLYMER *

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When hydrocarbons of the butadiene series are kept at a constant temperature, a peculiar type of polymer is formed, a white amorphous mass which is insoluble in organic solvents and which can catalytically cause formation of a similar product in the presence of the original hydrocarbon. Kondakov[1] first observed the formation of such a product in biisopropenyl. Lebedev[2] called this type of hydrocarbon polymer of the butadiene series a spongy polymer. This spongy polymer is also frequently called an autopolymer in the chemical literature because it is formed without change of temperature and without a catalyst.

Harries[3], Lebedev, Koblyanskiĭ, Khokhlovkin[4] and others observed the formation of a spongy butadiene polymer at a temperature not above 20° C, and also the sensitivity of this reaction to the action of light and to the duration of the process, especially in its first stages before the formation of sizable quantities of spongy polymer.

The formation of spongy polymer was studied in greater detail by Khokhlovkin. Koblyanskiĭ and Piotrovskiĭ observed the formation of spongy polymer during the thermopolymerization of butadiene at 40° to 60° C, and Koblyanskiĭ and Rokityanskiĭ observed its formation during the polymerization of butadiene in the presence of sodium and carbon dioxide. In this case, because of the complete inhibition of polymerization of butadiene by organic sodium compounds which are destroyed by the carbon dioxide, the authors observed the formation of spongy polymer on the surface of the sodium.

In conclusion it should be noted that a substance similar to this spongy polymer is formed during the polymerization of chloroprene[5], and is known as ω-chloroprene polymer.

In the present work we shall describe the results of a more detailed investigation of the formation of spongy butadiene polymer.

EXPERIMENTAL PART

The authors have proved (in coöperation with M. I. Lyutina) that the formation of spongy butadiene polymer is accelerated by the addition of a number of metals to butadiene. For example, the process is accelerated by the addition of iron, tin, nickel, aluminum, zinc, magnesium, barium, silver, gold, and other metals to the butadiene. On the contrary, the formation of spongy polymer was not observed on lead or on copper.

The formation of spongy polymer is also accelerated by the addition of crystals of inorganic salts, such as potassium dichromate and sodium chloride to the butadiene. It was proved also that, in the absence of iron, the spongy

* Translated for Rubber Chemistry and Technology by Alan Davis from the *Journal of Applied Chemistry*, Vol. 22, No. 5, pages 518–523 (1949).

polymer is formed, not only at temperatures up to 60° C, but also at 80°, 90°, and even 106° C. This disproves the contention of Harries[6], who related the formation of spongy polymer to the conditions of polymerization of the hydrocarbons of the butadiene series at room temperature.

The formation of spongy polymer on iron is of the following general character. In the first stage of polymerization (at 60° C this stage lasts 10–15 days), although butadiene is polymerized to the cyclic dimer of ethenyl-1-cyclohexene and to a soluble polymer, on neither iron nor on glass are there any visible indications of the formation of spongy polymer.

After this initial period, various small nuclei appear on iron, and these continue to grow and ultimately fill the whole ampoule with spongy polymer. In specially conducted experiments we established that, when iron or any other substance which accelerates the formation of spongy polymer is introduced into the butadiene, the acceleration of the polymerization process depends on this formation. These data were obtained by extracting the polymer with benzene.

It turns out that, after extraction of the dissolved polymers and spongy polymer from the total quantity of dimer obtained, the dimer and dissolved polymer are removed in quantities corresponding to those which are formed during the polymerization of butadiene without iron.

In our preceding work[7] it was shown that, after careful extraction of oxygen and peroxides from the butadiene and from the apparatus during the thermopolymerization of butadiene, only the butadiene dimer is formed and no thermopolymer. Following the experimental technique described in the previous work[7], we proved that, by careful extraction of oxygen and peroxides from the butadiene, the apparatus, and the iron (which is introduced into the ampoule), no spongy polymer is formed on the iron.

The results of these experiments are given in Table 1.

Table 1

Formation of Spongy Polymer on Iron with and Without Extraction of Oxygen and Peroxides

Polymerization times (days)	Experimental conditions	Quantity of spongy polymer formed (% of butadiene)
15	With careful extraction of oxygen and peroxides	None
	Without extraction of oxygen and peroxides	5.5
25	With careful extraction of oxygen and peroxides	None
	Without extraction of oxygen and peroxides	29.8
46	With careful extraction of oxygen and peroxides	None
	Without extraction of oxygen and peroxides	75

Thus, during the formation of spongy polymer, an accelerating action is exerted by the oxygen and peroxides. However, the presence in the butadiene of a surface layer of most of the metals or certain crystalline substances accelerates the formation of spongy polymer. The activating action of these substances is a process resulting from the adsorption of the peroxides from the butadiene undergoing thermopolymerization onto the surface of the metal or salt, as a result of which the molecules are activated, with formation of spongy polymer.

If this hypothesis is correct, then when the surface area of the iron or other metal increases, the formation of spongy polymer is accelerated only up to a definite surface area of the iron, that is, it is accelerated only to the point where

TABLE 2

FORMATION OF SPONGY POLYMER FOR DIFFERENT SURFACE AREAS OF IRON (EXPRESSED AS PERCENTAGE OF BUTADIENE)

Series of experiments	Surface area of iron (in sq. cm.)								
	0.07	0.23	0.44	1.26	2.49	6.14	9.87	12.26	24.50
1st	1.0	1.3	—	5.5	9.7	7.8	—	7.0	7.7
2nd	1.4	1.8	1.8	7.3	11.0	14.4	13.0	15.3	—
3rd	1.6	—	1.6	3.0	4.6	—	6.4	—	—

the surface of the iron corresponds to the adsorption of a unimolecular layer of the total quantity of peroxides on the surface of the iron. A further increase of the surface area of the iron does not appreciably affect the formation of spongy polymer on the iron, since activation of the peroxide molecules has already started. We performed a number of experiments to ascertain the influence of the surface area of the iron on the formation of spongy polymer. The experiments were conducted without carefully removing the oxygen and peroxides from the butadiene, the apparatus, or the iron. In these experiments the butadiene used had been regenerated from its tetrabromide, purified with alkali, and dried by calcium chloride and metallic sodium. In all the experiments the total amount of butadiene was disregarded. Identical weights of butadiene were introduced into ampoules of standard size, and thereby the

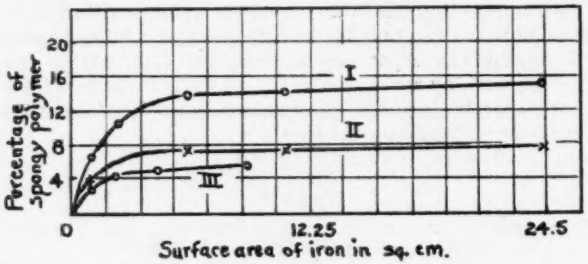


FIG. 1.—Effect of surface area of iron on the formation of spongy polymer.
I—First series.
II—Second series.
III—Third series.

influence of the weight of the butadiene could be ignored. In all the experiments 5 grams of butadiene was used. The dry purified butadiene was condensed into a graduated ampoule, from which it was again evaporated and condensed at 80° into ampoules containing iron of different surface areas. The experiments were conducted at 60° ± 0.10° C. The polymerization process lasted 15 days. The results of the experiments are given in Table 2 and are shown in the graph. It is evident from the graph that an increase of surface area of the iron accelerates the formation of spongy polymer only up to a certain limit. For example, in all the experiments a weight of butadiene equal to 5 grams was used, and an increase of the surface area of the iron to an area greater than 2.5 sq. cm. did not result in the formation of any more spongy polymer from the butadiene. Consequently, when this surface area is reached, adsorption of the peroxides from the butadiene in the form of a unimolecular layer on the surface of the iron is assured.

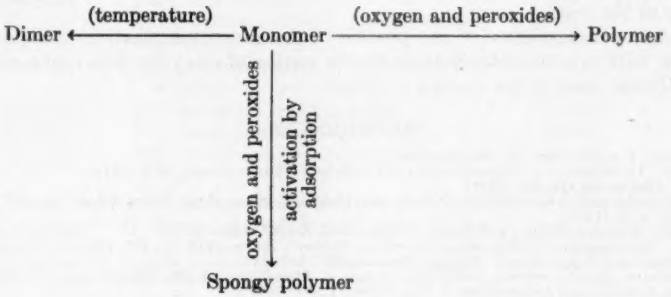
To prove these assumptions, we performed experiments in which polar substances which do not inhibit the polymerization reaction were added to the

butadiene. These experiments were based on the following considerations. If our assumption was correct that, in the formation of spongy polymer, the metallic surface acts as an adsorbent for the peroxides, then by adding polar substances to the butadiene, there is formed a protective layer on the surface of the iron which inhibits adsorption of the peroxides, and consequently inhibits formation of spongy polymer. For such substances we selected organic acids. According to published data[8], benzoic acid has no accelerating effect on the decomposition of peroxides. The experiments showed that when 0.001 per cent of benzoic acid, and iron having a surface area of 1 sq. cm. are added to butadiene, no spongy polymer is formed on the iron. These results were also obtained by the addition of stearic acid and oleic acid with iron to the butadiene. Finally, by adding benzoyl peroxide and iron to the butadiene, we proved experimentally that peroxides accelerate the formation of spongy polymer on iron. By adding only iron to the butadiene, we observed the formation of spongy polymer after 10–15 days at 60° C, though a very insignificant quantity was formed. Adding 0.076 per cent by weight of benzoyl peroxide to butadiene, we observed the formation of spongy polymer at 60° C, and when 0.9–1.0 per cent by weight of benzoyl peroxide was added to butadiene under the same conditions, the butadiene was converted into spongy polymer.

INTERPRETATION OF THE RESULTS

On the basis of these experiments, it was established that a necessary condition for the formation of spongy butadiene polymer, as well as for the formation of rubberlike butadiene polymers, is the presence of oxygen or peroxides. The formation of spongy polymer, in contrast to the formation of soluble polymers, is accelerated by the addition of metals (except lead and copper) and certain crystalline substances to the butadiene. When these substances are added, the formation of spongy polymer takes place at practically the same temperature as does the polymerization process. Removal of oxygen and peroxides from the butadiene and from the apparatus, even when iron is added to the butadiene, completely inhibits the formation of spongy butadiene polymer. The basis of this formation of spongy polymer must be regarded as an independent tendency of the polymerization process which proceeds parallel to the formation of cyclic butadiene dimer and the soluble rubberlike butadiene polymer. However, if only temperature affects the formation of butadiene dimer, and only oxygen and peroxides affect the formation of soluble butadiene polymer, then the additional activation of peroxides by adsorption on specific surface areas is still necessary for the formation of spongy polymer.

Thus, the thermopolymerization of butadiene can be expressed in the following way:



The accelerating action of the surface area of iron on the formation of spongy polymer continues up to the specific limit; besides, if, on the basis of the experimental data obtained, an approximate calculation of the peroxide content of the butadiene is made, then one finds that in the butadiene used in this experiment, the content of active oxygen is about 1.10^{-5}–1.10^{-6} per cent. This agrees with data obtained experimentally by Talmud, Golding, and Aldakushkin[9]. By this calculation according to the equation:

$$G_N = \frac{1}{S_{\sim}N}$$

where G_N is the number of gram-molecules of the adsorbed substance during saturation of the adsorbed layer, N is the Avogadro number, and S is the area occupied by one polar group in the saturated layer.

The same quantity of peroxides as of organic acids (22×10^{-6} sq. cm.) was used, and according to the calculation there are either 2 or 4 polar groups in the peroxides.

By such calculations, we determined that the addition of 0.001 per cent by weight of benzoic acid to butadiene, where the total quantity of butadiene is 5 grams and the surface area of the iron is 1 sq. cm., forms a unimolecular layer on the surface of the iron, and this prevents the formation of spongy polymer.

Finally, the acceleration of the formation of spongy polymer on iron when benzoic peroxide is added to the butadiene is clear proof of the validity of our assumptions concerning the formation of spongy polymer.

ACKNOWLEDGMENT

The present work was completed under the direction of G. G. Koblyanskiĭ, whose memory the author deeply respects.

CONCLUSIONS

1. It is shown that the formation of spongy butadiene polymer is accelerated by the addition to the butadiene of most metals and certain crystalline substances. This spongy polymer is not formed on lead or copper.

2. It is shown that the formation of spongy polymer on iron takes place at practically any polymerization temperature.

3. It is proved that in the absence, both in the butadiene and in the apparatus, of oxygen and peroxides, no spongy polymer is formed, and also that peroxides accelerate the formation of spongy polymer.

4. It is proved that the activation of the formation of spongy polymer by iron is of an adsorptive nature, and the formation of spongy polymer on iron can prevent the formation of a unimolecular layer of a polar substance on the surface of the iron.

5. An outline scheme of the process of thermopolymerization of butadiene is given, with experimental data on the formation of its cyclic dimer, of a rubber-like polymer, and of the spongy polymer.

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THE SULFONATION OF NATURAL RUBBER *

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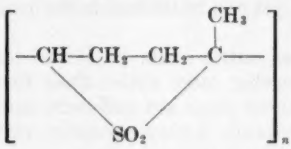
Like many olefins[1], natural rubber is capable of reacting with sulfur dioxide, with formation of a sulfone. The reaction is a chain reaction which is started by certain catalysts. The structure of the rubber sulfone is:



and the theoretical proportion of sulfur is 24.2 per cent.

Table I gives some experimental results obtained in the reaction of rubber with sulfur dioxide.

TABLE I

SOME EXPERIMENTAL CONDITIONS IN THE REACTION OF RUBBER WITH SULFUR DIOXIDE

(Four per cent solution of rubber hydrocarbon. Concentration of sulfur dioxide in the reaction mixture, 25 per cent by volume)

Solvent	Percentage of catalyst (based on the rubber)	Time of reaction	Temperature of reaction	Percentage of sulfur in the product
Benzene	5% diazoaminobenzene	20 min.	0	12
Chloroform	5% diazoaminobenzene	20 min.	0	13
Benzene	1% lithium nitrate	24 hr.	10	16
Benzene	4% lithium nitrate	24 hr.	10	20
Benzene	5% silver nitrate	24 hr.	10	11
Benzene	0.2% nitric oxide (NO)	0.5 min.	0	18
Benzene	0.4% nitrous anhydride (N_2O_3)	1 min.	0	16
Chloroform	0.2% nitrous anhydride	1 min.	0	12
Benzene	0.5% nitric acid	1 min.	0	17
Benzene	0.5% sodium nitrite (aqueous solution)	1 min.	0	18
Benzene	5% benzoyl peroxide	3 hr.	0	0.6
Benzene	5% ascaridol+trace of hydrogen chloride	1 min.	0	17
Benzene	5% *tert*-butyl hydroperoxide	0.2 min.	0	19
Benzene	5% tetraline hydroperoxide	0.2 min.	0	18
Benzene	5% 1-hydroxycyclohexyl hydroperoxide	0.2 min.	0	18

It was found that diazoaminobenzene and its derivatives are catalysts of this reaction. If about 5 per cent of catalyst (based on the rubber) and about

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25 volume-per cent of sulfur dioxide are added to a rubber solution, the reaction is evident by a pronounced gelling of the solution. After some minutes at 0° C, it is possible to isolate products containing close to 12 per cent of sulfur, *i.e.*, 0.4 mole of combined sulfur per isoprene unit. The catalyst acts only in the presence of a little oxygen. Diazoaminobenzene can likewise be used as a catalyst of the reaction between solid rubber and liquid sulfur dioxide.

CATALYSTS OF THE REACTION OF RUBBER WITH SULFUR DIOXIDE

It was found by Hilton[2] that lithium nitrate and silver nitrate catalyze the reaction between rubber and sulfur dioxide. Lithium nitrate, which in the proportion of 2 per cent on the rubber, is a very effective catalyst, gives products containing 20 per cent of sulfur after the reaction has continued for 24 hours at 0° C. This catalyst can be utilized in the reaction of both solid rubber and rubber in solution.

Furthermore, the gases, nitric oxide (NO) and nitrogen tetroxide (N_2O_4), were found to be considerably more active than these nitrates. Very small proportions of either of these gases are sufficient, and subsequent addition of sulfur brings about immediately a very energetic reaction between the rubber in solution and the sulfur dioxide.

Supposedly the catalytic effect of lithium nitrate and of silver nitrate is related to the analogous effect of nitric oxide and of nitrogen tetroxide, for presumably these gases are liberated slowly from the nitrates under the influence of sulfur dioxide, and perhaps also of moisture.

Likewise very small percentages of aqueous solutions of sodium hydroxide and of nitric acid catalyze the reaction between rubber and sulfur dioxide, and in these cases too it may be assumed that nitric oxide and nitrogen tetroxide are evolved.

Tetralin hydroperoxide *tert*-butyl hydroperoxide, and 1-hydroxycyclohexyl hydroperoxide are very active catalysts. A small percentage, based on the rubber, added to a solution of the latter, causes a violent reaction, with formation of products containing up to 20 per cent of sulfur. Benzoyl peroxide is not an active catalyst under these conditions. As far as ascaridol is concerned, it is an active catalyst only in the presence of traces of hydrogen chloride.

As with the reactions between olefins and sulfur dioxide, the reaction between rubber and sulfur dioxide has a limiting temperature, which, when carried out in an autoclave with lithium nitrate as catalyst, is around 40° C. In practice, the reaction is maintained within the range of −10° to 15° C.

PROPERTIES AND APPLICATIONS

The properties of rubber sulfones depend to a great extent on their sulfur content. Up to 5 per cent of sulfur, the products are elastic; with higher sulfur contents they are leatherlike in character; with still higher sulfur contents they have the character of horn; finally with the highest percentages of sulfur they are hard and brittle.

These sulfones of rubber are very difficult to process because of their insolubility and their lack of thermoplasticity, which results from the number of intermolecular bonds. A sulfone containing 20 per cent of sulfur does not swell in common organic solvents, but it does dissolve in concentrated sulfuric acid and concentrated nitric acid. Rubber sulfones can be precipitated from their solutions by dilution with water.

A very promising application[3] is the production of fibers by extrusion through a perforated plate of a solution of rubber containing a hydroperoxide into a solution of sulfur dioxide. It is possible also to obtain films by a similar process.

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STATISTICAL KINETICS OF HEVEA RUBBER CYCLIZATION *

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INTRODUCTION

Standard chemical reactions can often be carried out, not only on the customary small organic molecules, but equally on regular, high molecular-weight polymers. In such cases statistical effects may sometimes be observed to influence both the kinetics and the final composition of the products, whereby light may be shed on the reaction mechanism and on the structure. In simple cases to identical adjacent repeating units of a polymeric chain cooperate in an individual irreversible reaction step, usually to achieve a ring structure. If the unit be denoted by I, and the polymer chain by I_n or

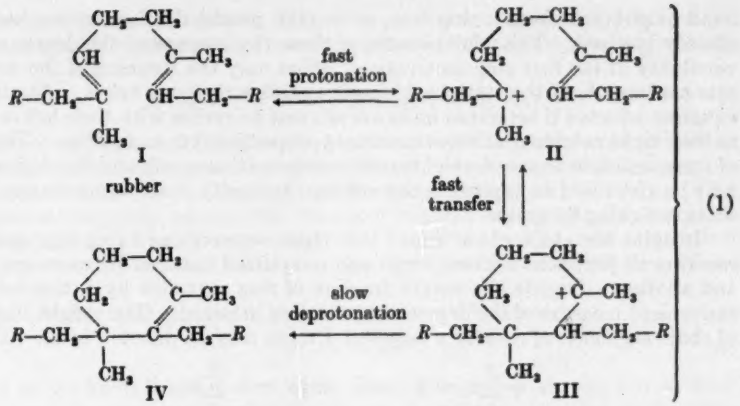
$$\ldots\text{—}I\text{—}I\text{—}I\text{—}I\text{—}I\text{—}I\text{—}I\text{—}I\text{—}\ldots$$

one may picture the following partly reacted section of a polymer chain:

$$\ldots\text{—}I\text{—}\overbrace{I\text{—}I}\text{—}I\text{—}\overbrace{I\text{—}I}\text{—}I\text{—}I\text{—}\ldots$$

in which the ringed couples are supposed to have reacted to form rings. Since the isolated I unit lying between the two rings shown is actually precluded from later reaction for want of a partner, the reaction cannot proceed to stoichiometric completion. Flory[1] calculated the proportion of these 'widows' (isolated units) in the final polymer to be $1/e^2$ (*i.e.*, 13.53 per cent) of the original I units, on the assumption that at each stage every couple of adjacent unreacted units has an equal chance of reaction. This result is practically independent of the degree n of polymerization, provided n exceeds about 15 or 20. Flory[1] and Wall[2] extended the calculation to the more complicated reactions of copolymers, and obtained results of importance for the experimental investigation of the arrangement of monomer units in the chain. Marvel and Levesque[3] and Gordon[4] pointed out that the cyclization of rubber is subject to this statistical effect and that analytical data on the unsaturation percentage of cyclized rubber by Fisher and McColm[5], which were previously unintelligible, actually provide the best known experimental verification of Flory's theory. The kinetics of this cyclization, catalyzed by 70 to 80 per cent sulfuric acid, were studied[4] by an emulsion technique on the basis of measurements in a diffusion gradient tube of the density of purified samples of the flocculated polymer. The mechanism supported by this work was:

* Reprinted from the *Proceedings of the Royal Society* (London), Series A, Vol. 204, pages 569–584 (1951).



(1)

Two of the original isoprenic units *I* (*viz.*, $-CH_2-C(CH_3)=CH-CH_2-$) in rubber here join to form a ring such as IV, and a theory was deduced for the statistical kinetic effect. This is due, of course, to the variations in status of an *I* unit as regards its chance of reacting, according to the number of its neighbors (0, 1, or 2) already reacted at time *t* during the reaction. The effect should manifest itself in a deviation from unity of the reaction order, initially to 1.5, and at the end of the reaction to about 1.16. Such deviations were not detectable by the gradient tube technique, and the present work was undertaken to confirm the rate equation by a more sensitive dilatometric method.

The chief value of the accurate confirmation actually obtained below lies in the consequent proof that the polymer forms part of the activated complex which determines the rate of the reaction. Such complexes involving polymers (*cf.* the propagation step of polymerization) are interesting as regards the entropy of activation and in other ways. Many simple diisoprenic terpenes such as dihydromyrcene cyclize under similar conditions as rubber, and undoubtedly by an analogous mechanism. Since they are not subject to the statistical effect under discussion, however, they do not lend themselves to this direct demonstration of their participation in the rate-controlling process. In fact, kinetic measurements on these terpene cyclizations are still not available, though the emulsion technique should render them quite feasible[6], and the polymer rubber has proved to be a suitable model compound for the lower terpenes, not only because of its advantageous statistical effect, but for its ease of manipulation also. Apart from throwing light on the role of the polymer in the mechanism, the measurements here reported strengthen the conclusions concerning the part played by the sulfuric acid. The fair correlation between the reaction rate and Hammett's acidity function previously noted is quantitatively confirmed. The conclusion that deprotonation rather than protonation is rate-determining still appears to hold, though one of its supports is weakened by a reduction in the accepted frequency factor resulting from these more precise measurements.

DERIVATION OF THE STATISTICAL KINETIC EQUATION

It will be assumed that cyclization is initiated by suitable activation on an isoprene unit *I* in the rubber chain, followed by attack of this unit on its right-

hand neighbor to form a ring (*e.g.*, as in (1)), provided this neighbor has not already cyclized. The relative rates of these two steps, and the degree of reversibility of the first step (activation), affect only the meaning of the overall rate constant k_s of the statistical kinetic equation deduced below. Nor is the equation affected if activated units are allowed to cyclize with their left as well as their right neighbors at rates remaining proportional to each other. The law of mass action in terms of weight concentrations is assumed, and the derivation may be visualized as applied to one rubber chain with N (Avogadro's number) units, weighing 68 grams.

Imagine the chain cut at time t into chain segments and ring segments by severing all junctions between rings and uncyclized units, or between one ring and another. Denote the weight fraction of ring segments by r, this being a convenient measure of the degree of cyclization attained. The weight fraction of chain segments of exactly k adjacent I units may be denoted by i_k. Thus:

$$r + \sum_1^\infty i_k = 1 \quad \text{and} \quad dr/dt = -\sum_1^\infty di_k/dt \tag{2}$$

The exact rate equation for the growth of r is:

$$dr/dt = k_s \sum_1^\infty i_k(k-1)/k = k_s(1 - r - \sum_1^\infty i_k/k) = k_s(1 - r - (N_e/N)) \tag{3}$$

This is deduced by noting that rings are formed from the various chain segments comprising k adjacent I's at rates proportional to i_k (law of mass action), but also proportional to $(k - 1/k$, because each segment contains one out of its k units which is ineffective. The ineffective unit is the one at the right end, whose activation cannot lead to cyclization for want of a right-hand partner. In the second equality of (3), the term $\sum_1^\infty i_k/k$ represents the deviation from first-order kinetics, and in the third equality this is equated to N_e/N, where N_e is the total number of chain segments irrespective of length.

The weight fraction i_k has a rate of change which is the balance of its rate of formation and rate of decay:

$$di_k/dt = k_s k \left(2 \sum_{k+2}^{\infty} i_n/n - i_k(k-1)/k \right) \tag{4}$$

formation decay

Thus its rate of change is proportional to the number k of I units involved. The term $k + 2$ under the summation sign indicates that the chain segment with k units can be created only from segments having at least two extra units. The multiplier $2/n$ affecting i_n applies, because activation of two only out of the n units in an n-chain is favorable to such a creation. For instance, a segment of five can be created out of one of nine units in the following two ways:

$$\overbrace{R—I—I—I—I—I—I—I—I—I}^{9}—R$$

First way: $R—I—I—R—\underbrace{I—I—I—I—I}_{5}—R$

or

Second way: $R—\underbrace{I—I—I—I—I}_{5}—R—I—I—R$

The term in (4) for the rate of decay is explained as the similar term in (3). One can simplify the system of Equations (3) and (4) by eliminating all fractions except r, i_1 and i_2:

$$dr/dt = k_s(1 - r - i_1 - i_2/2 - di_1/dt) \tag{5}$$

Further simplification, leading to the exact functional dependence of r alone on t, though theoretically possible, seems difficult. A very satisfactory approximate solution will now be derived by estimating the term N_c/N in (3). This solution is integrable, agrees with the exact solution asymptotically at the beginning ($r = 0$) and end ($r_f = 0.8647 = 1 - 1/e^2 = 1 - i_f$), and rests intermediately on a plausible physical picture of the approximate distribution of the segments.

If N_r is the total number of rings at any time t, we have:

$$N_r/N = \tfrac{1}{2}r \tag{6}$$

Let X be the fraction of the rings which are neighbored on the right by another ring, *i.e.*, a parameter measuring the degree of clustering together of the rings in the distribution of rings and chains during cyclization, so that:

$$N_c/N = (1 - X)N_r/N = \tfrac{1}{2}(1 - X)r \tag{7}$$

since the number N_c of chains is equal to the number of those rings which are not neighbored by a ring on the right. The rate Equation (3) becomes:

$$dr/dt = k_s(1 - r - \tfrac{1}{2}(1 - X)r) \tag{8}$$

At the beginning of cyclization, when r is very small, X must approach zero, while later as r grows, X grows. Putting X equal to zero, the initial rate equation becomes asymptotically:

$$dr/dt = k_s(1 - 1.5r), \quad \text{initial reaction (1.5 order)} \tag{9}$$

This law does not represent the further course of the reaction, *e.g.*, it brings cyclization to an end ($dr/dt = 0$) when $r = 0.6667$ instead of 0.8647. To find X approximately as an increasing function of r, one notes that the isoprenic unit lying just to the right of a ring may either be found cyclized with its right neighbor or not, and that X is the ratio of the probabilities of these two events. If we choose an isoprene unit entirely at random (without requiring it to lie to the right of a ring), the probability of it being found cyclized with its right-hand neighbor, the same as that of being found cyclized with its left neighbor, is $\frac{1}{2}r$. The probability of it not having cyclized with its right neighbor is $1 - (\frac{1}{2}r)$, and the ratio of the two events of interest is accordingly $r/(2 - r)$ for an entirely arbitrarily chosen unit. Assuming that this represents also the required ratio for a unit lying just to the right of a ring, an assumption probably near to the truth, there results:

$$X = r/(2 - r) \tag{10}$$

One can test this assumption at the end of the reaction by substituting (10) in (8) and putting dr/dt equal to zero. Solving for r, one obtains $r = 1$ instead of 0.8647 as the final degree of cyclization. It is clear that the clustering tendency X of the rings at the end of the reaction has been somewhat overestimated by (10), but a mere 10 per cent adjustment in X is required, as shown by the term 0.902 in (11), to obtain the correct asymptotic behavior ($r_f = 0.8647$) in (12):

$$X = (r/(2 - r)) \times (e^2 - 3)(e^2 + 1)/(e^2 - 1) = 0.902r/(2 - r) \tag{11}$$

and by substitution in (8):

$$dr/dt = k_s(1 - r - (\tfrac{1}{2}r)(1 - 0.902r/(2 - r)) \quad (12)$$

On the basis of the underlying physical meaning, there is little reason to suppose that X will deviate at all seriously from (11) in the earlier parts of the reaction, where in any case the Equation (12) becomes progressively less sensitive to such deviations. Further adjustments are accordingly not warranted, and the desired approximate rate Equation (12) is integrated to:

$$t = F(r) - F(r_i) = k_s\{ - 0.3569 \log(0.8674 - r)/(1.187 - r) \\ -0.5909 \log((1.0257 - r)^2 - 0.259) - 0.4846\} - F(r_i) \quad (13)$$

where r_i in the integration constant $F(r_i)$ denotes the initial degree r of cyclization. It is shown in (5) that experimental data confirm this equation in preference to a first-order law.

THE EQUILIBRIUM POLYMER AND ITS STRUCTURE

The statistical kinetic theory of Equations (3) and (4) and the statistical thermodynamic theory of Flory[1] can be unified and checked against each other. The following infinite series is postulated:

$$di_1/dt = - \sum_{3}^{\infty}(S_n/n)(di_n/dt) \quad (14)$$

and permissible values of the coefficients S_n found by comparing coefficients of i_n in Equation (4), using successively the values $k = 1, 2, 3$, etc. The result is:

$$S_n = 2(1 + S_3 + S_4 + \cdots + S_{n-2})/(n - 1) \quad (15)$$

which is precisely Flory's equation (3) for the number S_n of units I out of an n-chain which is the average "widowed" in the whole course of the reaction. Integration of (13) yields:

$$i_1 = i_f - \sum_{3}^{\infty} S_n i_n/n \quad (16)$$

which correctly asserts that the current fraction i_1 of widows at time t is equal to the final value minus the fraction yet to be widowed from among all the chain segments remaining at that time. The distribution function of rings and chain segments during, or of R and I units at the end of the reaction, though implicit in Equations (3) and (4), has not been solved. A reasonable model with a calculable distribution function for the statistically cyclized rubber can be derived. It correctly contains 13.53% I units and 86.47% R's by weight, *i.e.*, about three rings to an isoprene unit, in a random copolymer structure schematized thus:

$$—RIRRIRRRRIRIRRRRRRIRIRRRIRRRRRIR— \quad (17)$$

As cyclization is irreversible, two I's must not come together. The model is constructed by imagining $3 \times 13.53 = 40.59$ per cent of a monomer IR, consisting of an isoprenic unit flanked on its right by a ring, to copolymerize randomly with 59.41 per cent of a monomer R. The distribution function of this model is readily calculated, and from it the interesting conclusion can be drawn that 51.54 per cent by weight of the unit RIR can be cut from the cyclized rubber by judicious splitting of links in the polymer chain (17). This shows the usual representation of cyclized rubber as $(R)_n$ to be quite inadequate.

EXPERIMENTAL

About 1300 grams of acid latex was compounded, essentially as described in previous reports[7] by mixing Dunlop 60 per cent Hevea rubber latex with a stabilizer and sulfuric acid. Four kinetic runs were undertaken over a period of 4 months by following the volume change of the latex during cyclization in the thermostatically controlled Pyrex dilatometer shown schematically in Figure 1. At elevated temperature the stem of the dilatometer passed through a

TABLE 1

Run no.	Temperature (° K)	Percentage concentration c of H_2SO_4	Rate constant k_2 (min.$^{-1}$)
1	298.5	78.1	0.00021
2	332.7	78.1	0.01732
3	338.5	78.1	0.02652
4	357.2	70.9	0.013
5	298.5	79.2	0.0002985
5	298.5 corrected to	78.1	0.000192

lid covering the thermostat (not shown), and the control was to one-thirtieth degree or better. The fifth run recorded in Table 1 was intended as a check, being based on a latex compounded from a different shipment, and by its excellent concordance proves that the rates are reproducible. The run numbered 4 was on a latex obtained from the acid latex of runs 1 to 3 by dilution with a known amount of water, to check the influence of acidity on rate (see later).

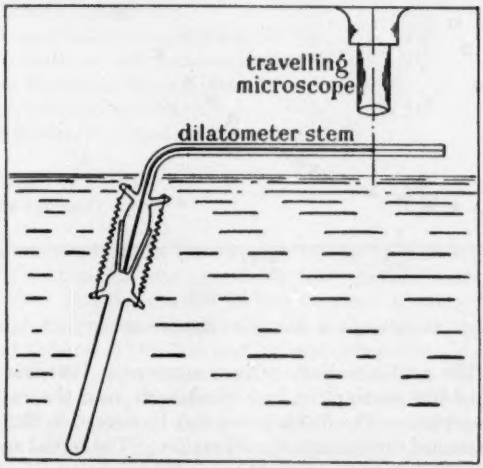


FIG. 1.—Sketch of dilatometer.

The full details of measurement and checks quoted hereafter refer to the model run 3, comprising 66 measured points taken consecutively during one day. Detailed calculations were also performed on runs 2 and 5, and gave on all accounts substantially equally good agreement. In particular, the results fitted the statistical law better than a first-order equation.

The acid latex was stored in a dropping funnel at −20° C in a frozen condition. When required for filling the dilatometer, it was allowed to attain about

+10° C, stirred and evacuated to 1 inch of mercury for about 10 minutes. The evacuation was found essential to avoid the evolution of a small amount of gas during the dilatometric run. The dilatometer was filled and weighed, thus giving the initial density D_f^L of the latex. Simultaneously, a sample was drawn for titration of the acid content by alkali, and one flocculated for the determination in a diffusion gradient tube of the density D_0^P of the pure polymer phase at that instant. The weight percentage of rubber in the latex was slightly variable from run to run, owing to creaming effects of the heavy sulfuric acid phase on the light rubber phase. The effect of this on the overall composition of the large remaining latex bulk was negligible. The correct rubber content of the latex in the dilatometer was calculated in two different ways, on the assumption that creaming did not disturb the kinetically significant concentration $c(H_2SO_4/(H_2SO_4 + H_2O))$ of the acid. The first calculation was based on D_0^L and D_0^P,

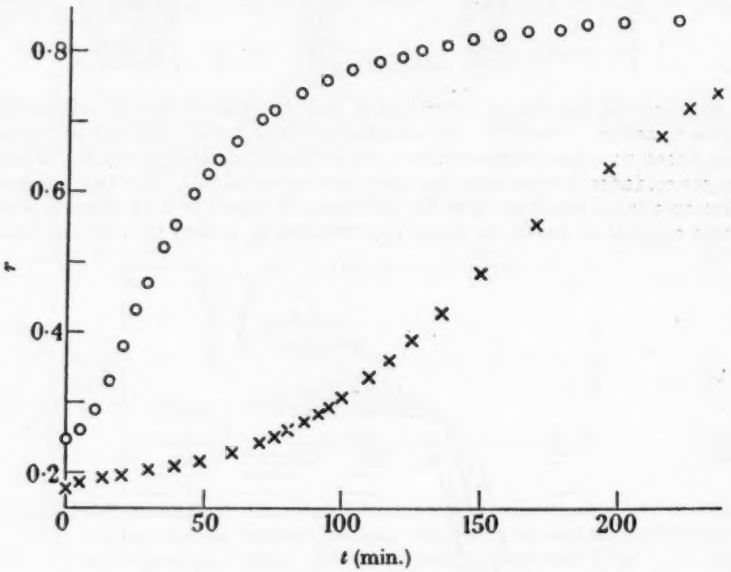


FIG. 2.—Plot of degree of cyclization r against t min. ○, run 3: ×, run 4.

the second on the acid titration. Close agreement between the two values obtained justified the assumption just mentioned, and the value based on the titration was accepted. The dilatometer was immersed in the thermostat, and 6 minutes was allowed for thermal equilibration. The initial zero reading of the latex meniscus in the stem was then taken. The density D_f^P of the polymer at this instant was still close to D_0^P, the small change during equilibration being readily estimated from the subsequent rate. The isothermal contraction during the run was followed by noting the meniscus displacement M (cm.) from its original zero position to its final M_f. Since the total volume contraction during cyclization was less than 2 per cent, no stem correction was necessary for the cold latex drawn from the dilatometer stem into the dilatometer during the run. This omission of this very small and uncertain correction favors a first-order law over the statistical one, since it must cause a drop in the apparent reaction order.

Curves showing the reaction progress r against time t are plotted in Figure 2. For this purpose r was calculated from the linear relation (21) linking it with M. Table 3 gives all the observed values of M and t for run 3.

CHECK ON THE VALIDITY OF THE TECHNIQUE

The rate constants of the dilatometric runs 2, 3 and 4 agree within a factor of two to three with the previous work based on measurement of D^P in a gradient tube. This would be accounted for by an error of about 2 per cent in the sulfuric acid concentration c, but agreement is actually somewhat better, because the present rate constants k_2 refer to the statistical law and take cognizance of the induction period (see later), while the previous work employed first-order constants k_1. The much less satisfactory agreement of the k_2 values for the runs at 25.3° C with the previous rate constants reflects a lower activation energy than previously found, a discrepancy discussed later.

TABLE 2

DETAILS OF MEASUREMENTS FOR RUN 3

Immersed volume of dilatometer	V	$=3.754_2$
Rate of meniscus movement with latex volume	dM/dV^L	$=128.7$ cm.$^{-2}$
Initial density of latex at 25° C	D_i^L	$=1.4985$ g./ml.
Rubber content calculated from compounding, by weight		19.1%
Actual accepted rubber content (see text)		16.3%
Mean mass of rubber in V during run (calc. at 25° C)	m	$=0.926$ g.
Observed final meniscus displacement	M_f	$=9.45$ cm.
Density of (slightly cyclized) starting polymer (25° C)	D_0^P	$=0.920\pm0.001$
Estimated polymer density at first meniscus reading (25° C)	D_i^P	$=0.922\pm0.002$
D_i^P calculated from Equation (18) as a check		$=0.920_4$
Final density of cyclized polymer (25° C)	D_f^P	$=0.981_2$
Mean apparent coefficients of cubical expansion measured:		
H_2SO_4 (79%)		$=0.00055_1$ ° C^{-1}
Initial latex (slightly cyclized)	C_i^L	$=0.00053_7$ ° C^{-1}
Final latex (fully cyclized)	C_f^L	$=0.00046$ ° C^{-1}

As an independent check on the validity of the present method, the total measured volume contraction was calculated from M_f and compared with the separately measured density change of the polymer phase proper. To this end the practically stationary final density D_f^P of the polymer was measured in a gradient tube at the end of the run, and D_f^P calculated from M_f for comparison with the measured value, *i.e.*, the corrected value based on D_0^P. As shown in Table 2, D_f^P calculated from M_f according to Equation (18) was 0.920_4, while D_0^P was found 0.920 ± 0.001 and D_f^P estimated therefrom 0.922 ± 0.002. This agreement shows satisfactorily that the dilatometric volume change of the latex reflects the volume change of the rubber particles in it during cyclization, especially if it is borne in mind that small effects due to nonrubber components in the latex have been neglected and that a large number of measurements enter into the calculation. In particular, the dilatometric volume change being measured at 65.3° C, but the polymer densities at 25.3° C ($\Delta T = 40°$ C), a correction was required for the difference of the apparent coefficients of expansion of the initial latex C_i^L and the final latex C_f^L. Thus, since the coefficient of expanison of the starting polymer (slightly cyclized rubber) was about 0.0005, but that of the fully cyclized rubber only about 0.0002, the volume contraction

of the latex at 65° C was about 16 per cent larger than at 25° C. The F^L values were measured in the same dilatometer over the same range T, so that disturbing effects such as the small expansion of the Pyrex dilatometer itself could be neglected. All the measurements are recorded in Table 2 and the formula employed was:

$$1/D_f^r = 1/D_f^p - \frac{M_f - \Delta TVdM/dV(C_f^r - C_f^L)}{m(dM/dV)} \qquad (18)$$

On the assumption that the deprotonation step in (1) determines the rate, an upper limit previously estimated for the basic strength of rubber (pK_a of the carbonium ion III < about −8) is here experimentally confirmed. Thus, since the volume change during cyclization must be associated very largely with the proton transfer step which precedes the slow deprotonation, the protonation and transfer equilbria in (1) cannot lie more than a few per cent over to the products; otherwise the slow contraction observed on the latex would correspondingly fall short of the contraction of the rubber phase during cyclization.

DISCRIMINATION BETWEEN STATISTICAL KINETIC AND FIRST-ORDER LAW

It will now be shown that the main central portion of run 3, covering about 78 per cent of the measured volume change and 50 per cent of the total cyclization reaction, conforms definitely to the statistical Equation (19), with $F(r)$ as defined in (13), rather than to the first-order law (20). The comparison is exhibited in Table 3 by confronting the observed times $t_{obs.}$ with times t_s calculated from (19) and t_1 calculated from (20):

TABLE 3

DISCRIMINATION BETWEEN FIRST-ORDER AND STATISTICAL CYCLIZATION KINETICS

Point no.	Meniscus displacement M (cm.)	Time (min.)		
		$t_{obs.}$	t_s calc.	t_1 calc.
0	0.0	0	11.51	9.81
1	0.148	4	12.12	10.51
2	0.220	5	12.39	10.85
3	0.315	6	12.78	11.31
4	0.562	9	13.81	12.51
5	0.655	10	14.19	12.97
6	0.761	11	14.68	13.51
7	1.002	13	15.74	14.75
8	1.134	14	16.33	15.45
9	1.270	15	16.97	16.17
10	1.407	16	17.62	16.92
11	1.714	18	19.16	18.65
12	1.865	19	19.95	19.53
13	2.020	20	20.76	20.44
14	2.324	22	22.45	22.31
15	2.588	24	23.98	24.00
16	2.777	25	25.14	25.25
17	3.064	27	26.97	27.22
18	3.195	28	27.84	28.15
19	3.338	29	28.84	29.38
20	3.871	33	32.80	33.31
21	4.126	35	34.87	35.44
22	4.344	37	36.77	37.36
23	4.571	39	38.84	39.43
24	4.765	41	40.75	41.29

TABLE 3—*Continued*

Point no.	Meniscus displacement M (cm.)	Time (min.)		
		$t_{obs.}$	t_2 calc.	t_1 calc.
25	4.949	43	42.63	43.14
26	5.226	46	45.65	46.09
27	5.407	48	47.79	48.13
28	5.649	51	50.87	51.02
29	5.806	53	53.00	53.02
30	5.968	55	55.33	55.16
31	6.166	58	58.39	57.96
32	6.351	61	61.46	60.76
33	6.541	64	64.87	63.81
34	6.706	67	68.06	66.68
35	6.841	70	70.94	69.17
36	7.018	74	74.93	72.68
37	7.177	78	78.87	76.12
38	7.390	84	84.80	81.20
39	7.675	93	94.11	89.10
40	7.777	97	97.91	92.36
41	7.900	102	102.93	96.62
42	8.018	107	108.29	101.17
43	8.096	112	112.15	104.47
44	8.192	117	117.32	108.91
45	8.229	120	119.47	110.75
46	8.302	124	124.02	114.68
47	8.347	127	127.00	117.25
48	8.403	131	130.91	120.73
49	8.464	136	135.54	124.89
50	8.543	141	142.24	130.96
51	8.558	145	143.54	132.27
52	8.613	149	148.89	137.20
53	8.681	155	156.21	144.27
54	8.721	159	160.84	149.08
55	8.723	162	161.22	149.35
56	8.761	165	165.98	154.50
57	8.772	168	167.39	155.98
58	8.804	172	173.44	161.10
59	8.838	177	177.43	167.38
60	8.879	187	184.36	176.08
61	8.916	192	191.45	186.36
62	8.954	200	199.58	200.00
63	8.962	205	201.73	203.45
64	9.007	220	213.49	231.63
65	9.349	316	∞	∞
66	9.450	393	∞	∞

$$k_2 t_2 = F(r) - F(r_i) + x \tag{19}$$

where

$$r_i = 0.2468, \quad F(r_i) = 0.3052, \quad x = 0.3052, \quad k_2 = 0.02652 \text{ min.}^{-1}$$

$$k_1 t_1 = -\log(1 - r) + \log(1 - r_i) + x' \tag{20}$$

where

$$r_i = 0.1879, \quad -\log(1 - r_i) = 0.7261, \quad x' = 0.7368, \quad k_1 = 0.010307 \text{ min.}^{-1}$$

The calculation of the times and of the r's are respectively slightly complicated because a small initial portion of all the runs, and a very small final portion of the runs at elevated temperature, conformed with neither law. Thus in fitting the experimental $t_{obs.}$ and the r values calculated from the measured meniscus displacements M to Equations (19) and (20), ideally only the rate constants k_2 and k_1 require adjustment. In practice, however, two small addi-

tional adjustments have to be made in both cases to allow for the initial and final deviations. These adjustments do not conceal any favored treatment of either law. Thus the first adjustment concerns a displacement of the time origin by an amount x or x', respectively, as shown in the last two equations, to allow for an induction period, which is visible in Figure 2 and whose significance is discussed in §7. Probably fortuitously, these adjustments cancelled the integration constants $F(r_i)$ and $\log(1 - r_i)$ in runs two and three within experimental error, so that the main part of the reaction proceeded along the theoretical curve for $r_i = 0$ and absence of an induction period.

The meniscus movement reflecting accurately the volume change in the rubber phase, is therefore linearly related to the reaction progress:

$$aM = r - r_i \tag{21}$$

where for Equation (19), $a = 0.0669$, $r_i = 0.2468$; and for Equation (20), $a = 0.0897$, $r_i = 0.1879$. Ideally, the constant a should be fixed as $(r_f - r_i)/M_f$. However, the abnormality at the end of the reaction causes a slow volume change after (on the kinetic evidence) cyclization is complete, and thereby affects M_f and a. For Equation (19), $r_f = 0.8647$ and $(r_f - r_i)/M_f = 0.0654$, while 0.0669 gives the best fit. Again, for Equation (20) $r_f = 1$, the theoretical $a = 0.08593$, while $a = 0.0897$ gives the best agreement. The r_i values chosen correspond closely to those calculated from D_0^2 and the density (0.900) of uncyclized rubber. It is emphasized that after suitable adjustments in a and k_2 (but not k_1), variations in the assumed r_i of ± 0.1 leave the fit of Equation (19) practically, and that of Equation (20) exactly, unaltered, because of an invariantive property of the first order law. Table 3 lists the times $t_{obs.}$, and the times t_2 and t_1, respectively calculated from Equations (19) and (20), with the aid of (21).

After an induction period of about 20 minutes, 28 out of 49 consecutive values of t_2, covering an interval of 180 minutes, lie within 30 seconds of the experimental $t_{obs.}$, 12 points lie between ½ and 1 minute, 8 points between 1 and 2 minutes, and only one point between 2 and 3 minutes off. On the other hand, the t_1 values, while agreeing about equally well over the range from 20 to 70 minutes and again at 200 minutes deviate between 70 and 200 minutes smoothly up to a maximum of over 12 minutes from the $t_{obs.}$. These facts show not only that a conclusive experimental decision in favor of the statistical law (19) has been obtained, but also the high accuracy actually required for such a decision.

DEPENDENCE OF RATE ON ACIDITY AND TEMPERATURE

The usual Arrhenius plot of the runs listed in Table 1 is shown in Figure 3. The best straight line through runs 1, 2, 3 and 5 has been drawn, and from this the rate at 357.26° K and sulfuric acid concentration $c = 78.1$ per cent can be computed. When this is compared with run 4, at the same temperature but at $c = 70.9$ per cent, the relation:

$$\frac{d \log k_2}{dc} = 0.165 \tag{22}$$

is found between these two concentrations, in very good agreement with the value (0.17) obtained in the previous work, so that the correlation between reaction rate and Hammett's acidity function H_0 is confirmed[6]. The small correction of the rate of run 5, from the measured value at $c = 79.23$ to the desired value at $c = 78.1$, as shown in Table 1, is based on Equation (22).

The temperature dependence of the rate of cyclization agrees much less well with that previously reported, the activation energy calculated from runs 1, 2, 3 and 5 being 25.3 kcal. instead of 32.7, and the frequency factor 4×10^{14} min.$^{-1}$ instead of 3×10^{19}. The main reason for these deviations must be sought in the runs at 25.3° C, which showed much higher rates than predicted from the previous work. Two explanations may be advanced for these deviations. First, while the overall activation energy of 32.7 kcal. previously found referred to a temperature range between 25 and 100° C, the Arrhenius plots showed some definite curvature, and lower values can be calculated from the data falling within the range 25 to 65° C here studied. Thus the three points in the earlier work at 78.5 per cent acid in this temperature range correspond to 29.8 kcal., the two points at 72.6 per cent acid to 24.8 kcal. of activation energy.

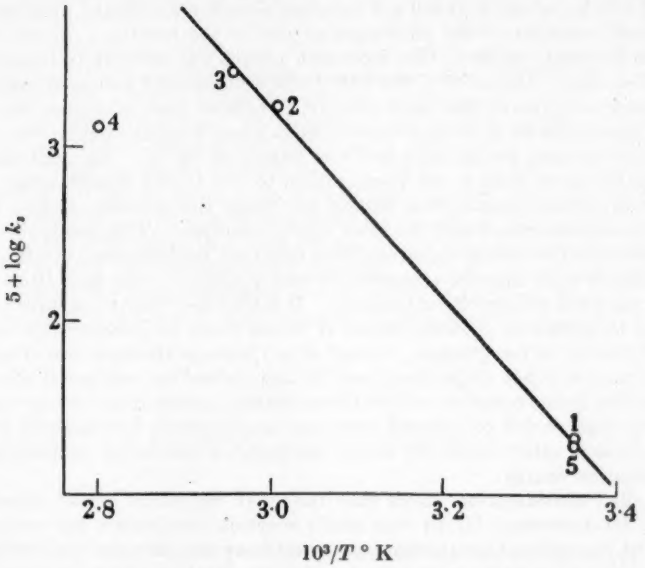


FIG. 3.—Arrhenius plot for runs 1 to 5. (For numbering, see Table 1.)

Secondly, the previous density technique was based on the assumption of a unimolecular law and was insufficiently sensitive to show the initial and final rate abnormalities observed in this work, and is accordingly regarded as less reliable in the calculations of the Arrhenius parameters of the cyclization step.

The only serious implication of the lowering of the Arrhenius parameters at 78.1 per cent acid and between 25 and 65° C which has thus been accepted is a weakening of the support previously derived from the exalted frequency factor for the rate control by the deprotonation step (as in scheme (1)) rather than by the first (protonation) step. It has been shown[4] that a very high-frequency factor such as 10^{19} min.$^{-1}$ could correlate only with a reaction step in which ionic charges were neutralized in the transition state, *e.g.*, a collision between the cyclocarbonium ion III and an HSO_4^- ion to produce IV and H_2SO_4. The new value of 4×10^{14} is now normal for a unimolecular reaction, though still very

high for a collision between an ion and a large uncharged molecule, such as occurs in the protonation step. Moreover, from the previous experience cited, the frequency factor may be expected to rise with temperature, and certainly with acid concentration c, so that considerably higher values could actually be experimentally realized. Since the deprotonation rate control is by no means an unusual mechanistic feature, and has been supported also by the influence of the structure of various terpene substrates on their approximately known cyclization rates, it is still the preferred mechanism though on weaker grounds in view of the reduced activation entropy.

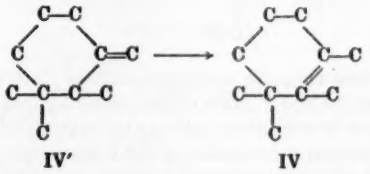
SMALL INITIAL AND FINAL RATE ABNORMALITIES

An induction period of reduced rate was observed in the runs at elevated temperature. While, as Figure 1 shows, this was particularly marked at the reduced acidity of run 4, it did not interfere even there with the determination of the rate constant of the later regular part of the reaction. Trials showed that the detailed course of this induction period was accurately reproducible for a given latex. As at 25° C the initial rate abnormality was much reduced in importance relative to the main change, it follows that whatever the mechanism responsible for it, it must be subject to a much smaller activation energy. The abnormal rate period split into two phases at 25° C. The first phase on bringing the latex from a low temperature to 25° C and equilibrating, was a "burst" of volume contraction, lasting for about 100 minutes, at first several times too fast compared with the later regular reaction. This slowly died down to a rate below the normal value and then rose back to the normal in a few hours. These effects were likewise reproducible and confined to the first 10 to 20 per cent of the total measured contraction. Whether the "burst" occurred also at elevated temperature is uncertain, as it would there be obscured by the time of equilibration of temperature, though it is visible in the slow run (Figure 1). Its significance is not understood, and it may indeed be connected with some side reaction in the complex colloidal latex system, rather than with cyclization. The induction period of reduced rate may be connected with the rate of diffusion of the acid catalyst into the rubber particles[8], a conclusion supported by its low activation energy.

Detailed consideration shows that the small induction period cannot reasonably be accounted for by any chain reaction mechanism for cyclization. The most plausible chain mechanism would have the effect of cyclization of a couple of isoprene units spread to an adjacent couple, and so on all along the segment of chain remaining uncyclized. This mechanism would arise, for instance, if the deprotonation step of one ring became the protonation step of the adjacent unit. Such a scheme would bear only superficial resemblance to the acid-catalyzed chain polymerization of olefins, though a number of radical reactions of rubber have been formulated as similar chain sequences of cyclizations involving two units at a time (see later). The correlation of cyclization rate with Hammett's acidity function H_0 indicates a proton transfer from the acid to the rubber; this step would actually have to be rate controlling in any chain mechanism, as the alternative of deprotonation control (as in (1)) would not be available. A chain mechanism controlled by the activating protonation would, however, have a higher reaction order than here observed, indeed as high as two under the simplest assumptions. This will be appreciated from the simple argument that at half-cyclization ($r = 0.5$), the rate of cyclization would, compared with the starting rate, be halved because the number of units available for activation would be halved, and then again be halved because

each activation would, on average, lead to rapid cyclization of chains of only half the original length. Thus it does not appear possible that any chain mechanism would produce rate equations that could approach the excellent agreement with experiment achieved by the nonchain mechanism (1) and Equation (19). Moreover, the number of widowed units in a chain mechanism would fall to a much smaller proportion than the 13.5 per cent of Flory's theory for a nonchain mechanism, which is in close agreement with Fisher and McColm's analytical results on cyclized rubber[5].

Turning now to the rate abnormalities at the end of the reaction, these reflect a step subsequent to cyclization proper, since the density of the rubber increases gradually well above the end point approached kinetically during the main part of the reaction. At the highest temperatures previously employed (90 to 100° C), at which there is some danger of oxidative side reactions, densities up to 0.990 had been recorded. It has since been found that, at $c = 78$ per cent and 60° C, ten different latexes gave definite end products whose densities lay between 0.984 and 0.985, even after several hours' continued maintenance under these reaction conditions. The reproducibility of this "cyclized rubber" must be regarded as high, since most synthetic polymers are sold commercially on density specifications only to the second decimal place. The polymer density approached by the main part of the reaction in the high-temperature dilatometer runs was near to 0.980. The nature of the subsequent shift to 0.984–5, which took several hours to complete, might be sought in a cross-linking or in a prototropic displacement of the remaining double bonds. The latter alternative seems more likely, since there appears to be no marked decrease in solubility or swellability. There is some intrinsic probability that the thermodynamically less stable γ-terpene form IV′ is formed first, and the subsequent reaction might thus be its transformation to the β-form IV:



IV′ IV (23)

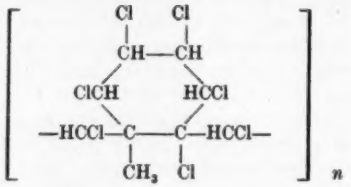
Some spectroscopic evidence has been quoted earlier[7] for the presence of rings IV′ in cyclized rubber, though a detailed confirmation of the reaction (23) will require further spectroscopic examinations to be made. (23) would account, not only for the small volume decrease found, but also for the marked rise in softening point, because the semicyclic double bond would confer mobility on the ring IV′, while the endocyclic bond in IV would cause considerable stiffening.

In the runs at 25° C, the reaction was too slow to carry the polymer in practice beyond a density of 0.974.

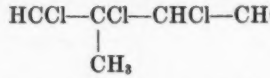
CONCLUSION

The emulsion technique of making kinetic measurements on latex rubber, presents, among other advantages, much higher precision than earlier methods. The average reaction order of the present measurements being approximately 1.25, the conclusive discrimination from a 1.0 order law necessitated not only the highest attainable precision, but also a careful investigation of the mathe-

matical effects of possible errors in all the parameters involved. As an illustration of the difficulties of the earlier methods, the simple unaccelerated vulcanization of rubber with sulfur may be cited. Several investigators, working with bulk (as distinct from latex) rubber, assessed the order of this reaction at values ranging from zero to over 1. The correct value is undoubtedly unity, as shown by the analysis of adiabatic rate measurements[9], in agreement with the most likely mechanism. The rate-determining step being the splitting of a sulfur ring without aid from the polymer, statistical kinetic effects are not encountered in vulcanization. Numerous examples of statistical kinetic and equilibrium effects probably do exist in rubber chemistry. Farmer[10] has described several reactions of other substances (SO_2, Cl_2, maleic anhydride) with two neighboring units of rubber at a time. Statistical effects should apply to all these at equilibrium through the survival of uncyclized units; and wherever, in the absence of chain mechanisms, rubber enters the rate-controlling step, Equation (13) may be expected to apply. As an example, the empirical formula $(C_{10}H_{11}Cl_7)_n$ has been accepted by Le Bras and Delalande[11] in support of the structure:



which is closely analogous to IV. Uncyclized units, probably



should accompany these rings, in amounts varying from 13.5 per cent down to negligible proportions, as the kinetic chain varies in length from units (single cyclization act without lateral propagation) to large numbers. The diagnostic value in studies of reaction mechanism of the appropriate statistical analysis is thus evident, though the experimentally attainable precision is here still the limiting factor.

The present work has confirmed the postulated mechanism by its demonstration that the rubber polymer enters the rate determining step in cyclization. It has established that this reaction is essentially not an intermolecular cross-linking, but a reaction between couples of neighboring units in a long chain, 13.5 per cent of which escape from cyclization. Indeed, a purely kinetic proof has now been furnished of the basic fact that rubber is a polymer, containing long chains of identical units.

SUMMARY

Rubber cyclization provides a useful illustration of statistical effects intervening in the reactions of long-chain polymers. Analogously to known cyclizations of simple diisoprenic terpenes, each individual cyclization act links two adjacent isoprene units in the rubber chain into a six-membered ring. However, some of the units remain stranded between neighboring rings and escape cyclization for want of a partner. Thus the final polymer has a copolymer

structure of 86.5 per cent of diisoprenic rings and 13.5 per cent of uncyclized monisoprenic units. This result is derived from a statistical theory of Flory, and has previously found accurate experimental verification. The bearing of this statistical effect on the reaction kinetics has now been studied for the first time. Dilatometric experiments on rubber emulsions in sulfuric acid have shown that the cyclization reaction conforms in the main with a statistical cyclization law much better than with a first-order equation uncorrected for the survival of stranded units. High accuracy was required for this experimental distinction, whose importance lies in the implicit proof that the polymer units participate in the rate-determining transition complex, in accordance with the accepted proton transfer mechanism. A kinetic proof has incidentally been furnished for the fact that the rubber polymer contains long chains of identical units. When handled by an emulsion technique, this polymer can provide a useful "model compound" for its simpler terpene analogs.

Certain rate abnormalities have been observed, including an induction period of reduced rate, probably connected with diffusion effects. A small volume change subsequent to the cyclization reaction may reflect a prototropic double-bond shift. The activation energy and entropy are found to be lower than in previous work, an effect traced in part to a curvature of the Arrhenius plot. The known dependence of cyclization rate on Hammett's acidity function H_0 is quantitatively confirmed.

ACKNOWLEDGMENTS

The writer wishes to record his gratitude to Professor C. K. Ingold for his encouragement and advice, to the Dunlop Rubber Company for permission to publish this paper, and to L. A. Wragg for assistance with the experimental part.

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[6] Gordon, *Ind. Eng. Chem.* **43**, 386 (1951).
[7] See also British patent 634,879.
[8] Gordon, "Hevea Rubber: Cyclization Kinetics and Proton Affinity", Thesis, London Univ., 1949.
[9] Gordon, *J. Polymer Sci.* **3**, 438 (1948).
[10] Farmer, in "Advances in Colloid Science", Interscience Publishers, New York, 1946, p. 302.
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KINETICS OF CYCLIZATION OF HEVEA LATEX *

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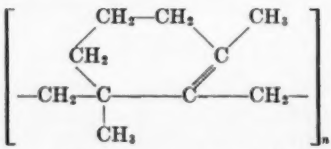
Rubber hydrocarbon and the natural proteins are typical products formed by living cells with synthetic skill as yet unmatched by man. The hallmark of this skill is the low entropy and energy of activation appertaining to natural syntheses[1] in which "improbable" and ordered transition states are achieved, undoubtedly through the harnessing of surface forces. When natural proteins[2] or rubber are exposed to the action of rather brutal catalysts, they are transformed into the thermodynamically more stable denatured protein and cyclized rubber, respectively. The brutality of these transformations is betrayed by the high frequency factors and activation energies, that is, the highly jumbled and energized transition states through which the polymers are forced to relinquish some of the free energy invested in them by living tissues. Nevertheless, those struggling with the difficulties peculiar to colloid and polymer chemistry will find encouragement in the evidence presented here to show that, through its cyclization, rubber provides a model reaction for the kinetic understanding of similar reactions among its low molecular weight analogs.

When Hevea rubber, or under some conditions synthetic polyisoprene[3], is exposed to the action of heat[4] of a silent electric discharge[5], cathode rays[6], or acidic catalysts of the Lewis type[7] or Bronsted type[8], it is progressively resinified. The resin, like the parent rubber, has the empirical formula $(C_5H_8)_x$. In the course of this isomerization reaction the refractive index, density, and softening point of the polymer increase, whereas its unsaturation decreases, and a definite end point is attained in these changes. Chemical theories of the reaction have attributed the disappearance of double bonds to cyclization, in particular to the mutual saturation of double bonds, or their saturation at the expense of broken C—H bonds. The structure of the cyclized rubber has been formulated as either monocyclic or polycyclic[9], but a monocyclic structure is supported by the present work. It will be shown that substantially identical monocyclic rubber has been obtained by Fisher, Staudinger, and other workers, including the writer, by a variety of methods, despite doubts entertained on this uniformity by earlier workers. The most widely accepted structure[3] for a monocyclic polymer is that of D'Ianni and co-workers:



(1)

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 386–393, February 1951. This paper was presented at the International Meeting of the Division of Rubber Chemistry of the American Chemical Society at Cleveland, Ohio, October 11–13, 1950. The present address of the author is the Royal Technical College, Glasgow C 1, Scotland.

As kinetic experiments on the cyclization reaction had not previously been reported, this work was planned primarily to fill this gap. When carrying out studies of rubber reactions on emulsions of rubber prepared directly from latex without coagulation, advantages accrue as when passing from bulk or solution to emulsion polymerization. Moreover, the oxidative degradation to which rubber is prone if coagulated, washed, and milled prior to chemical reactions is avoided. When, after suitable stabilization, Hevea latex is converted without coagulation to an emulsion of rubber in a medium of 60 to 80 per cent sulfuric acid, one obtains smoothly and reproducibly an emulsion of cyclized rubber. This process was discovered independently by van Veersen in Holland[10] and by the writer[11]. Other examples of the emulsion technique are the hydrochlorination[12] and atomic chlorination[13] of rubber. For a fuller account of the kinetic technique used for the cyclization reaction, the thesis[14] on which this paper is based may be consulted.

EXPERIMENTAL TECHNIQUE

Table I shows the compositions and titration data of two typical latexes used. These were compounded from the four ingredients whose water contents

TABLE I

COMPOSITION OF TYPICAL LATEXES

Water content of ingredients (%)			
Uncompounded latex	38.33		
Lubrol-W solution	58.4		
Aqueous H_2SO_4	21.6		
Concentrated H_2SO_4	0.5		
Weights (grams) for latex used in runs	B1 and B2	C3	
Uncompounded latex	39.2346	25.0440	
Lubrol-W solution	2.9158	1.5740	
Aqueous H_2SO_4	8.2314	5.3922	
Concentrated H_2SO_4	43.6450	39.3278	
Extra water	—	0.23 ml.	
Calculated composition (grams)			
Total compounded latex	94.0268	72.57	
Total H_2SO_4	49.007	43.38	
Total H_2O	19.616	12.09	
Acid on medium (c)	72.68%	78.2%	
Acid on total (%)			
Calculated	53.02	59.8	
Found	53.04	59.54, 59.58 (duplicates)	
Details of check titration		Duplicates	
Weight of latex aliquot (grams)	3.9933	3.9026	3.6354
Normality of NaOH	2.086	2.083	2.083
cc. of NaOH (uncorrected)	20.81	22.75	21.21
Back titration equivalent	−0.12	−0.04	−0.05
Temperature correction	−0.01	—	—
Buret correction	—	—	—
Corrected volume of NaOH	20.69	22.71	21.16

are listed at the head of the table. The stabilizer was Lubrol-W[15], an ethylene oxide condensation product nonionic in water though probably ionized in the acid medium used. Samples of each latex (0.7 to 1.0 cc.) were sealed under 5 inches of mercury of air in Hysil ampoules and heated for measured times, t, in a thermostat controlled within 0.04° C. The content of each ampoule was, flocculated immediately after t minutes by pouring it into 25 cc. of a mixture of

acetone and water (equal volumes), under vigorous mechanical stirring, to produce a flocculate of 0.1- to 1.0-mm. particle size. A small amount of flocculate was collected and washed by suction on a microfilterstick carrying a No. 2, Whatman filter paper. The purified polymer was then not dried, but a small amount was pressed between microscope slides in steam at 100° C for 4 minutes. The density of the consolidated transparent central portion of the pressed polymer was found by cutting it into small parts, which were wetted with alcohol and transferred into a density gradient tube. The application of the gradient tube to measurements on polymers has been described by American workers[16]. The method was here improved by adapting simplified Berg im-

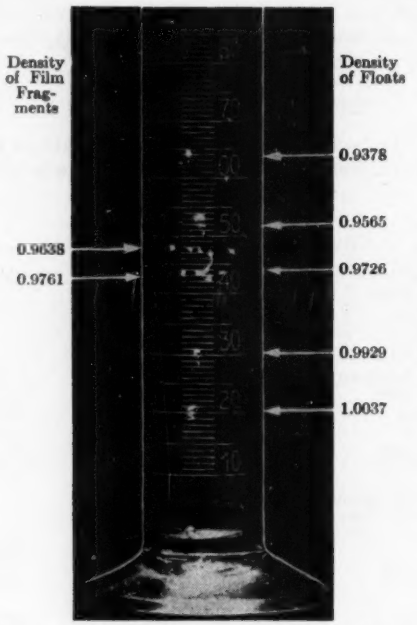


FIG. 1.—Gradient tube with glass floats. Film fragments are from two successive samples of run C2.

mersion hydrometers or glass floats[17] as reference standards in place of liquids or polymers of known density. The density of the glass floats was found essentially by the method of Berg to 0.0002 gram per cc.

The principle of the gradient tube is as follows:

Particles of the polymer to be measured are dropped under gravity into a thermostated 100-cc. measuring cylinder, in which a gradient of density is maintained by the interdiffusion of two miscible liquids. The particle comes to rest in a plane in which the density of the medium equals its own. A calibration curve, approximating a straight line over a large central portion is obtained by noting the scale readings for the glass floats. The density of partially cyclized rubber lies between 0.9 and 0.991 at 25° C and suitable gradients and were obtained from aqueous alcohol (density, 0.87) and aqueous lactic acid (density,

1.03). It was advisable to add small amounts of pyrogallol to both liquids, as otherwise oxidation of rubber or cyclized rubber caused a continuous increase in the density to be measured; an increase of 1 per cent per day was not unusual. The simplicity and accuracy of the density measurements are apparent from Figure 1. This shows the gradient tube with the glass floats and several film fragments from two successive samples taken from run C2.

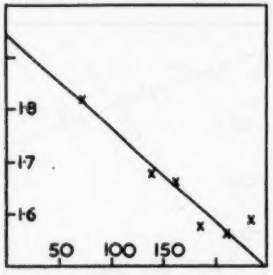


FIG. 2.—Run B1.
$3 + \log(0.991 - D)$ *vs.* t hr.

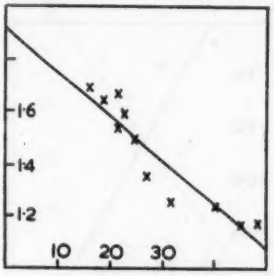


FIG. 3.—Run B2.
$3 + \log(0.991 - D)$ *vs.* t hr.

Because of the other sources of inaccuracy in making these kinetic measurements, it was not worth while to utilize fully the obtainable accuracy; measurements within ± 0.002 gram per cc. were adequate.

Four factors tending to interfere with the accuracy of measurements were studied[14] and eliminated where necessary by proper choice of conditions:

1. An oxidative side reaction and the possible effect of the sulfur dioxide produced
2. Gelling of latex during cyclization
3. Possible effects of the stabilizer
4. Diffusion of the acid phase into the rubber

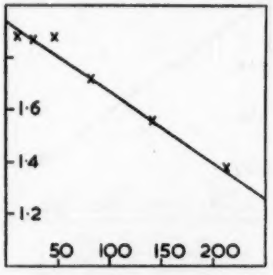


FIG. 4.—Run B3.
$3 + \log(0.991 - D)$ *vs.* t min.

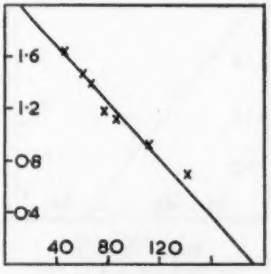


FIG. 5.—Run B4.
$3 + \log(0.991 - D)$ *vs.* t min.

That the latter is of no relevance to the measured rates is conclusively shown by the high activation energy of 33 kg.-cal. of latex cyclization. Experiments showed that when a 0.06-mm. film of rubber was exposed to 77.1 per cent sulfuric acid, diffusion of the acid into the rubber was largely rate-controlling.

Concentration effects and reaction order.—The kinetic runs fall into two series, one referring to acid concentration (per cent on medium of sulfuric acid and water) lying close to 72.5 and the other close to 78.5 per cent. Corrections were made for slight deviations from these two norms. The two series, B and C, respectively, conformed satisfactorily with a first-order law, as vouchsafed by the linearity of the usual plots. These took the form of $3 + \log_{10}(0.991 - D)$ versus time t, where D denoted the density at 25° C of the purified polymer and

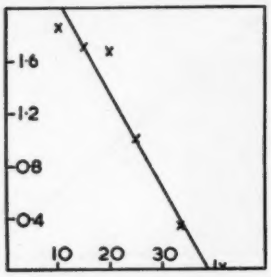


FIG. 6.—Run B5.
$3 + \log(0.991 - D)$ *vs.* t min.

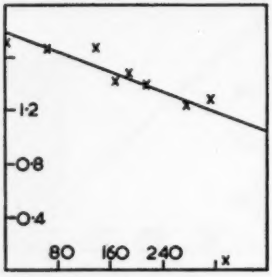


FIG. 7.—Run C1.
$3 + \log(0.991 - D)$ *vs.* t hr.

0.991 its final asymptotic density (Figures 2 to 14). The measured values of the latter parameter were between 0.987 and 0.991 for various fully cyclized samples, and the highest value found was adopted. The assumption underlying the plots is that the change in density is a linear function of the stoichiometric progress of cyclization. Evidence for this is found in the satisfactory extrapolation of the kinetic plots to the initial density of pure rubber. In this extrapolation the correct zero time lies about the 4-minute mark because of the initial heating-up perod of the ampoules.

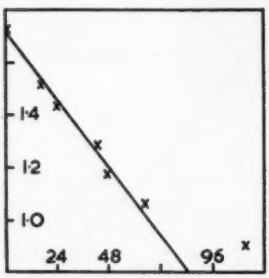


FIG. 8.—Run C2.
$3 + \log(0.991 - D)$ *vs.* t hr.

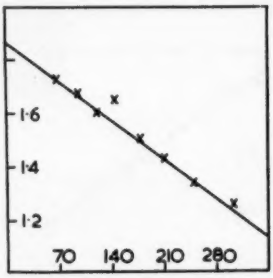


FIG. 9.—Run C3.
$3 + \log(0.991 - D)$ *vs.* t min.

The accepted density[18] of rubber (presumably at 20° C) has been close to 0.9065. The author finds, by the acidification and flocculation technique, that the density of rubber in latex is 0.900 ± 0.001 at 25° C and 0.9025 ± 0.001 at 20° C. The consolidation of the flocculate was omitted in the uncyclized rubber but was used directly in the wet state after washing on the filter stick. (Compression tended to produce spongy films.)

The low average density is probably more accurate for pure latex rubber than previously accepted higher values, and this testifies to the efficacy of purification when latex is brought to a high acidity, for a time insufficient to cause measurable cyclization, flocculated, washed, and the density of the flocculate found in a gradient tube containing pyrogallol as an antioxidant. It may be assumed that the acidification solubilizes all the protein from which it is otherwise

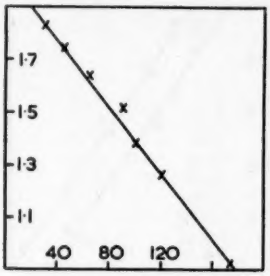


FIG. 10.—Run C4.
$3 + \log(0.991 - D)$ *vs.* t min.

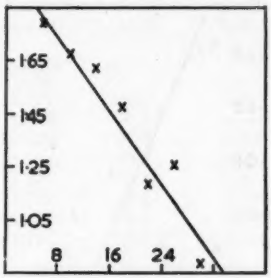


FIG. 11.—Run C5.
$3 + \log(0.991 - D)$ *vs.* t min.

notoriously difficult to rid latex rubber completely. The general adequacy of the first-order plots is apparent. Reproducibility varied somewhat from run to run: C1 was the least satisfactory and C4 perhaps the best, demonstrating first-order kinetics convincingly. All the measured points of run C2 are recorded in Table II as an example.

The best straight line was always drawn through the points covering the first 80 per cent of the reaction, as the last few points beyond that range sometimes deviated (C6, C8). Such errors might be due to an error in the assumed

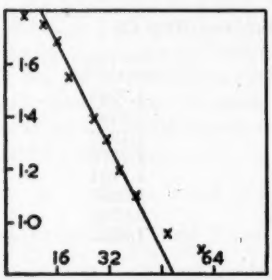


FIG. 12.—Run C6.
$3 + \log(0.991 - D)$ *vs.* t min.

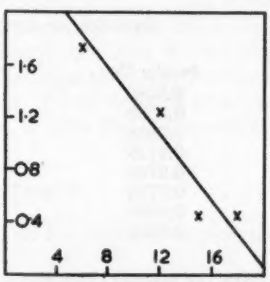


FIG. 13.—Run C7.
$3 + \log(0.991 - D)$ *vs.* t min.

final $D = 0.991$ or to real deviations from first-order kinetics predicted on statistical grounds as explained later. The constant, k, was found for each of the thirteen runs from the slope of its plot and expressed as $k = -2.303\, d \log_{10}(0.991 - D)/dt$ (Table III).

Arrhenius plots.—Before the final Arrhenius plots for the two series could be drawn for an evaluation of their activation energies, E, and frequency factors,

X, corrections were required for some small deviations in acid concentration from the mean values of 72.6 and 78.5 per cent, respectively, of most of the latexes employed. It may be mentioned that not all the runs were based on latexes separately compounded, but B1 and B2 were based on one latex, C1 and C2 on another, and C4, C5, and C7 on a third. The corrections and all details are recorded in Table III. The corrections were obtained from a preliminary Ar-

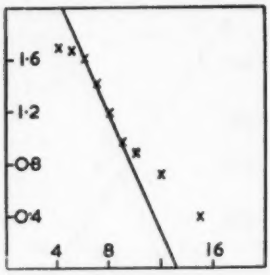


FIG. 14.—Run C8.
$3 + \log(0.991 - D)$ vs. t min.

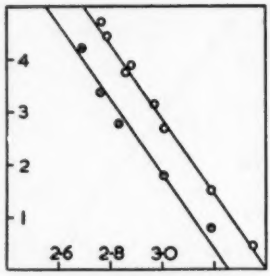


FIG. 15.—Arrhenius plot:
$5 + \log k$ vs. $10^3/T$.
⊙ = 72.6% H_2SO_4 (series B)
○ = 78.5% H_2SO_4 (series C)

rhenius plot of $\log_{10}k$ against $1/T$ (not shown), from which it appeared that for a given temperature $\log_{10}k$ differed by about 1.0 for the two series differing by 5.9 per cent acid on medium, independently of the temperature chosen. On this datum the constants were corrected for small deviations in acid concentration by assuming that $\log_{10}k$ varies linearly with this parameter over the small ranges concerned. The final corrected plot (Figure 15) shows good linearity,

TABLE II

DENSITY AS FUNCTION OF TIME FOR RUN C2

Density (D)	Time (t) (hours)	$3 + \log_{10}(0.991 - D)$
0.9380	0.83	1.7243
0.9580	16.70	1.5185
0.9638	23.30	1.4346
0.9716	42.30	1.2878
0.9760	47.80	1.1761
0.9795	64.80	1.0607
0.9820	111.4	0.9542
0.9804	143.0	1.0253

particularly for series C (78.5 per cent acid) for which more points were measured. Its regression line of $\log_{10}k$ on $1/T$ leads, on the basis of the usual calculation from the slope, to an energy of activation of 32.7 kg.-cal. The frequency factor, X, found from the intercept, is $10^{19.3}$ minutes^{-1}. The Arrhenius plot shows that the ten-fold decrease in rate in passing to runs B at 72.6 per cent acid on medium is due to a decrease in X rather than an increase in E. Whether E is exactly identical for both runs cannot, of course, be settled in the absence of absolutely accurate data. The line drawn through the points of series B was chosen as the best line parallel to the regression line through series

TABLE III

SUMMARY OF KINETIC RESULTS

Run	H_2SO_4 concn. (%)	Rate const. $k \times 10^5$	$5 + \log k$	$5 + \log k$ (Cor. to 72.6%)	Temp. (° C)	$1/T$ Abs. $\times 10^3$
B1	72.73	6.7	0.826	0.804	40.5	3.188
B2	72.73	67.8	1.831	1.808	59.85	3.003
B3	72.55	624	2.795	2.807	80.40	2.828
B4	72.53	2560	3.408	3.410	90.10	2.753
B5	72.70	16700	4.223	4.170	99.35	2.684
				(Cor. to 78.5%)		
C1	79.0	3.7	0.562	0.477	25.0	3.349
C2	79.0	41.7	1.620	1.535	40.5	3.188
C3	78.2	469	2.671	2.722	59.7	3.005
C4	78.5	1460	3.164	3.164	63.8	2.967
C5	78.5	8340	3.921	3.921	74.85	2.873
C6	78.3	5610	3.749	3.783	77.2	2.854
C7	78.5	30000	4.477	4.477	86.1	2.783
C8	78.3	49300	4.693	4.727	89.35	2.758

C, assuming E to be invariant, which gives a good fit. This procedure leads to a value of X of $10^{18.3}$ minutes^{-1} for an acid concentration of 72.6 per cent (runs B).

The ranges of concentration and temperature accessible to experiment are limited both by inconveniently slow or fast rates and by gelling and oxidative side reactions[14]. Since the accuracy of measurements of individual rate constants was sometimes doubtful to an extent of 20 or 30 per cent of their values, reliable values for the Arrhenius parameters could only be arrived at by spreading the measurements over a wide range of temperatures (60° to 70° C). Owing to the high temperature coefficient—about 3.8 for a 10° interval—of the cyclization reaction, the measured velocities thus ranged over a factor of 10^4.

Pilot experiments have shown the approximately linear variation of $\log k$ with acid concentration to which reference was made above. The theoretical sanction for this fact is found in the work of Hammett and others discussed later. On the assumption of this linear relationship, the data of the two series, B and C, can be combined in a single general rate equation covering variations of the unimolecular rate constant of cyclization of rubber latex as a function of temperature and sulfuric acid concentration, c, over the ranges suitable for technological exploitation:

$$\log_{10} k = 6 + 0.17c - 7105/T \qquad (1)$$

k is given in minutes^{-1} and T (as throughout) as the absolute temperature.

REACTION MECHANISM OF CYCLIZATION

Statistical theory of cyclization.—If the cyclization of rubber depends on the coöperation of couples of adjacent isoprene units, some units will become "widowed"—that is, they will be excluded from cyclization by virtue of the fact that their two potential partners (neighbors) have already reacted, each with its other partner. Flory[19] has calculated on statistical ground that in an irreversible reaction of this type, the final composition of the polymer will correspond to the presence of $100/e^2 = 13.53$ per cent of widows. Cyclization will fall short of stoichiometric completion by this percentage and the final

unsaturation will be:

$$\left[0.5\left(1-\frac{1}{e^2}\right)+\frac{1}{e^2}\right]\times 100 = 56.8\%$$

of the original, instead of 50 per cent as at stoichiometric completion. This result is in striking agreement with unsaturation measurements by Fisher and McColm on rubber cyclized in bulk, under conditions similar to the present latex technique, which gave 57 per cent unsaturation[8] by three different methods. The structure of cyclized rubber must, accordingly, be a "copolymer" of isoprene units (I) and a ring (R) consisting of two isoprene units. The calculated ratio of these units is almost exactly one I to three R in the statistical cyclized rubber. An approximate calculation[14] reveals that over 50 per cent of the cyclized polymer should be present as the unit (RIR), and this shows the usual representation of cyclized rubbers as $(R)_n$ to be inadequate.

A kinetic theory of the statistical effect has been proposed[14], and has led to the following integrated equation giving time t as a function of r, the stoichiometric degree of conversion (weight fraction of the rings formed):

$$t = -k\{0.3569\log(0.8647-r)/(1.187-r) + 0.5905\log[(1.0257-r)^2-0.259] + 0.4846\} \quad (2)$$

Within the accuracy and reproducibility of the density technique here described this equation approximates the first-order law implicit in the treatment described. A more sensitive dilatometric technique, however, is leading at present to an accurate confirmation of Equation 2 as will be reported[20]. It also appears likely from this further work that unsaturation changes may occur after the monocyclic structure is completely formed.

Rate and acidity function.—The reported kinetic mesurements permit mechanistic deductions from which important conclusions may be made concerning the structure of cyclized rubber. For instance, a chain mechanism of cyclization is rendered improbable, but a proton transfer mechanism is established through a correlation of the rates with Hammett's acidity function H_0. The background to this function and to the wide range of olefin reactions pictured to proceed by carbonium ion mechanisms has been admirably expounded[21]. Hammett defined an acidity function thus:

$$H_0 = pKa + \log(C_B/C_{BH^+}) \quad (3)$$

where pKa is the acidity constant

$$pKa = -\log(a_H a_B/a_{BH^+}) \quad (4)$$

of an uncharged Brønsted base, B; a is an activity and C a concentration. Though originally defined in terms of indicator equilibria, the function is also known to represent the variation with concentration of rate constants of conversions of a base substrate to its conjugate carbonium, so that

$$\frac{-d\log k}{dH_0} = 1 \quad (5)$$

Such correlation with rate measurements has so far been confined to the very dilute and very concentrated acid ranges. The present work narrows the kinetic no man's land by covering the range between 70 and 80 per cent sulfuric acid for the cyclization reaction of rubber. The existence of a single continu-

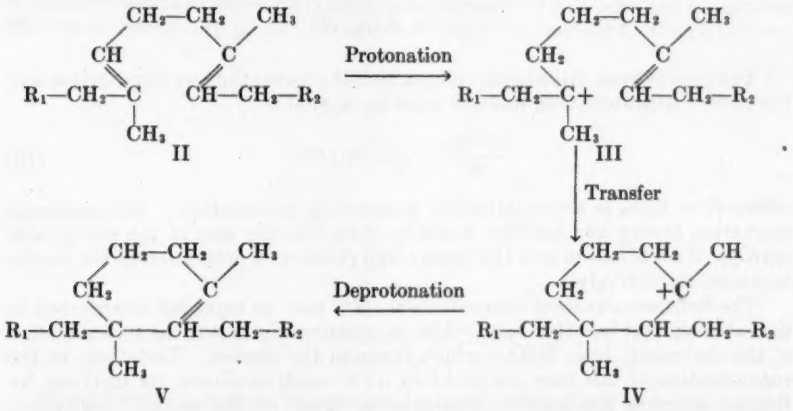
ous function, H_0, linking the regions of aqueous and autoproteolytic ionization, would seem to indicate a fluid linkage pattern in the solvent sulfuric acid, causing rates and equilibria to depend less on the concentration of definite ionic species than on the basic affinity of the solution as a whole. From the measurements of cyclization velocity at 72.6 and 78.5 per cent, respectively, for latex cyclization:

$$\frac{-\Delta \log k}{\Delta H_0} = 1.25 \text{ (estimated error } = \pm 0.1) \qquad (6)$$

Comparing this with the semitheoretical Equation 5, the deviation is not considered serious in view of the experiences of other authors[22]. The approximately linear variation of H_0 with c over this range, moreover, accounts for the linearity already mentioned of $\log k$ with c. It may thus be said that the correlation of velocity of rubber cyclization with H_0—reflecting an enormous sensitivity to acid concentration hardly explicable in other terms—is sufficiently close to give strong support to the notion that the reaction proceeds by the protonation of the double bonds in rubber. The presence of a large amount of aprotic diluent in the reaction phase, as here the rubber hydrocarbon itself, would not be expected to result in any large solvent effect[23]. Moreover, as found for rubber cyclization, variations of rate with H_0 usually largely reflect changes in X rather than E—for example, in anionotropic rearrangements[24], in acetylation of quinones[23], and nitration of nitrocompounds[25].

RUBBER CYCLIZATION AS CARBONIUM ION TRANSFER REACTION

According to the carbonium ion theory[26], rubber, like other terpenes, may be transformed into structure V as follows:



The more general field of olefin reactions based on proton transfer steps displays a bewildering typological and topological variety. It has been discussed elsewhere, and a generalized reaction scheme has been presented[14]. The protonation step is almost universally and carbonium ion transfer always found to occur in the Markownikoff (M) sense, which is energetically highly favored over the Anti-Markownikoff (A) sense[27]. In sulfuric acid of less than 80 per cent strength, carbonium ion transfers (involving a second double bond)

are generally favored over attack by carbonium ions on unsaturated centers. In the proton-catalyzed cyclizations of terpenes, six-membered rings are favored whenever other mechanistic requirements are equal. Their final deprotonation step can usually occur at three different centers of structure IV (four-carbon prototropy) under varying conditions or simultaneously, to give α-, β-, or γ-cycloterpene structures (Table IV, structures XII to XIV). This variety has been fruitful of controversy. There can be little doubt that the essentially first-order kinetics of cyclization reflect the participation of the rubber molecule in the rate-controlling step. Two well known cases arise[21] according to whether the proton return to the medium in the last step is or is not relevant to the observed first-order kinetics of the over-all reaction. The question can be settled in the present instance both by reference to the abnormally high entropy of activation and to the approximately estimated rates of related cyclizations. The following scheme covers both cases as degeneracies of a single equation derived in the usual manner by the method of stationary states:

$$B + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CBH)^+ \xrightarrow{k_3} CB + H^+ \tag{7}$$

B represents the rubber acting as a base, and CB the cyclized product of the reaction. $(CBH)^+$ denotes the cyclized ion, IV, produced by carbonium transfer; this last step is included in the protonation itself for convenience. The common rate equation is:

$$\frac{d(CB)}{dt} = \frac{k_2 + k_3}{k_1 k_3}(B)(H^+) \tag{8}$$

The first case, exclusive rate control by protonation, arises if $k_3 \gg k_2$, so that

$$\frac{d(CB)}{dt} = k_1(B)(H^+) \tag{9}$$

The second case, mixed control by a mobile protonation pre-equilibrium and the rate of deprotonation, arises if $k_3 \ll k_2$, so that

$$\frac{d(CB)}{dt} = Kk_3(B)(H^+) \tag{10}$$

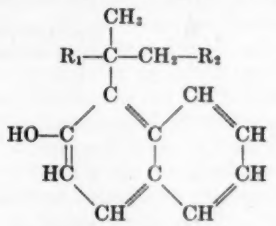
where $K = k_1/k_2$ is the equilibrium constant of protonation. The measured activation energy and entropy would be split into the sum of the energy and entropy of protonation and the energy and entropy of activation of the deprotonation, respectively.

The fictitious constant concentration (H^+) may be regarded as absorbed in the rate constant in either case. Also k_3 contains as a factor the concentration of the (solvated) base HSO_4^- which removes the proton. Variations in the concentration of this base are probably quite small as shown, for instance, by Raman spectral intensity[28]. Evidence in favor of the second mechanism (Equation 10) is found in the high activation entropy and in qualitative correlation between the rates of various terpene cyclizations. Detailed discussion[14] shows that an activation entropy of about +25 cal. per ° C, which corresponds to the measured frequency factors reported here, cannot be explained by disorder in the transition state involving merely rotational modes of the rubber substrate (when the double bonds are opened during protonation). This conclusion is borne out by an estimate of such an entropy contribution based on a

simple network theory. The positive activation entropy must be assigned to a charge-neutralizing reaction step[29]. It seems most likely that this step is the deprotonation reaction in which a positively charged cyclostructure (structure IV) collides with HSO_4^-. That the rate-determining step is deprotonation is strongly indicated by variations in cyclization rate of acyclic terpenes as a function of R_2 in structure IV (when R_1 = hydrogen).

Accurate kinetic measurements on terpene cyclizations are urgently needed. The activation energy of 32.7 kg.-cal. for rubber cyclization should be a valuable datum for comparison with those for other terpene cyclizations as they become available. A decrease of 13.5 kg.-cal. may be calculated in a number of cases for the proton affinity of a C=C, if a substituent methyl group is replaced by hydrogen[27]. This should raise correspondingly the activation energy of cyclization and accounts for the great difficulty[3] of cyclizing butadiene polymers.

The basic strength, or proton affinity, pKa of rubber, an important physicochemical constant, can be derived from a knowledge of the percentage protonation at a known H_0 (Equation 3). A rough guess at the percentage protonation of rubber may be based on a comparison with isobutene, which is likely to approach 100 per cent protonation[30] in 96 per cent sulfuric acid ($H_0 = -9.1$). If rubber is there protonated to between 10 and 90 per cent, its pKa would be between -8.1 and -10.1. Under the cyclization conditions of this work the protonation in the mobile equilibrium would affect 0.01 to 1 per cent of the double bonds. Support for the carbonium ion theory of rubber cyclization is in fact obtained by comparison of the chemistry of acidified rubber with isobutene whose conversion to carbonium ion has been spectroscopically proved[31]. For instance, isobutene alkylates phenols in presence of strong sulfuric acid. No explanation seems to have been given to the well known acid "condensation" of rubber with phenols—for example, β-naphthol[32]. Doubtless, the alkylation reaction proceeds through the rubber carbonium ion, leading to the structure:



VI

CYCLIZED RUBBER STRUCTURE IN LIGHT OF CYCLIZATION MECHANISM

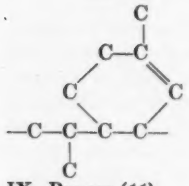
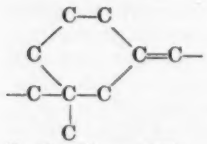
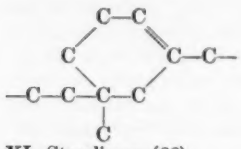
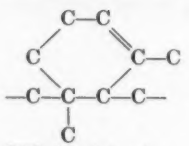
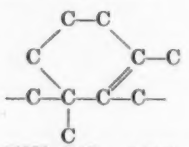
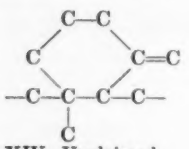
The structure suggested by previous investigators is illustrated and may be classified as follows:

Intermolecular cyclization
- Mutual saturation of double bonds
- Attack on saturated centers

Intermolecular cyclizations
- Monocyclic structures
- Polycyclic structures

TABLE IV

POSSIBLE SIX-MEMBERED RING STRUCTURES FOR CYCLIZED RUBBER

Structure[a]	Proton-ation sense	Group attacked	Substitution degree of C=C
 IX. Powers (*11*)	A	β-Methylene	3
 X. Staudinger (*33*)	M	Methyl	3
 XI. Staudinger (*33*)	M	Methyl	3
 XII. Unclaimed	M	α-Methylene or π electrons	3
 XIII. D'Ianni (*11*)	M	electrons	4
 XIV. Unclaimed	M	π electrons	2

[a] Structures requiring double bond shifts by prototropic steps independent of cyclization proper are not shown in the table.

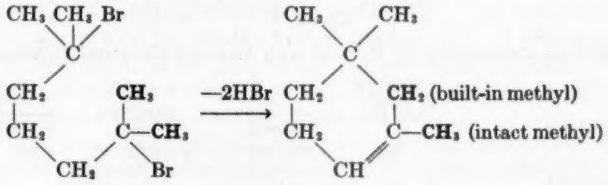
Intermolecular rings should result in a cross-linked highly insoluble type product. Staudinger and Widmer[33] and Fisher and McColm[8] found, however, that bulk or solution cyclized rubber prepared by various methods dissolves in numerous solvents, so the notion of a highly cross-linked structure must be abandoned. With Friedel-Crafts catalysts, insoluble products are obtainable, but probably are due to side reactions, since soluble products result when antioxidants are added to the reaction mixture[8].

The ready solubility of latex cyclized rubber[14] previously observed has now been found to be due to some oxidative breakdown attending dissolution. However, latex cyclized rubber is no less soluble than the starting latex rubber; the gel fraction is always highly swelled. Cyclization therefore, cannot be a cross-linking reaction. For acid catalyzed cyclization, a monocyclic product is indicated by the following new evidence arrived at in this work.

1. The reaction order close to unity is best in accord with a simple repetitive sequence of elementary steps.
2. The excellent agreement of Fisher and McColm's unsaturation measurements on acid-cyclized rubber with Flory's statistical theory.
3. The qualitative correlation of the reaction rates of cyclization of rubber and various monoterpenes can also be taken as supporting a monocyclic structure for cyclized rubber.

The structure of rubber, as that of other terpenes, favors formation of six-membered rings. Five-membered rings could result only from A sense protonation or (a reaction never yet observed) A sense carbonium ion transfer. Seven-membered rings could result only from attack on saturated centers. These mechanistic considerations, as well as the activation of double bonds by methyl substitution mentioned above, lend new mechanistic interest to the wide occurrence of isoprene as a building brick for natural products, a fact whose structural significance was early recognized by Ruzicka.

The six possible six-membered rings, together with relevant information, are shown in Table IV. Of these IX, proposed by Powers and quoted by D'Ianni and co-workers[3], is mechanistically least likely because it not only demands attack (during carbonium transfer) on the relatively stable β-methylenes, but it is also the only structure of the six to require A sense protonation. The two structures, X and XI, of Staudinger and Widmer[33] require attack on the methyl group, which is the most stable and resists all electrophilic reagents, for example, chlorine, that do not destroy the rubber skeleton. The structures were put forward more particularly to account for the cyclized rubber resulting from the dehydrohalogenation of rubber hydrohalides. They were explicitly supported[34] by supposedly analogous changes such as the dehydrobromination of 2,6-dibromo-2,6-dimethyl-*n*-heptane (structure VII).

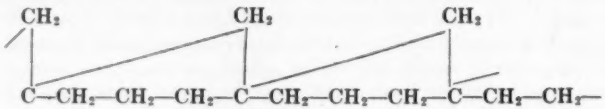


VII

One of the two equivalent methyl groups at the end of the molecule thus becomes built into the ring and the other remains intact. When passing to

rubber, one of these two methyl groups will be substituted with the rubber chain; the crucial question is: Which one? Staudinger implicitly assumes it must be the intact one, but since the alkyl substitution weakens the C—H bonds, it is the substituted methyl which is more likely to become incorporated in the ring. This leads to structure XII (Table IV) as the correct analog, or, if the alternative deprotonation steps are taken into account, possibly structures XIII and XIV also. The last three structures (XII to XIV) are, in fact, analogous to the alpha, beta, and gamma structures, respectively, of the simple cycloterpenes. They alone can result from M sense protonation and carbonium ion transfer according to the kinetic scheme proposed. Of the three, the unclaimed structure, XII, though consistent with known mechanistic requirements, is probably not in accord with infrared spectral analysis. The structures XII to XIV differ in the alkyl substitution degree of their double bonds, being disubstituted in XIV, trisubstituted in XII, and tetrasubstituted in XIII—the D'Ianni structure. D'Ianni and coworkers[3] supported this structure by the fact that infrared absorption due to the trisubstituted ethylenes in rubber disappears during cyclization.

A suggested intramolecularly polycyclic structure may now be discussed. Staudinger and Geiger[4] supposed that products obtained by the action of heat on rubber and by the dehydrohalogenation of rubber halides with zinc and hydrochloric acid are represented by the structure:



VIII

This is derived from X and XI (Table IV), and similar objections may be raised against it. The original evidence, based on low unsaturation values found by a bromine titration with an uncertain end point, may be discounted on the strength of Fisher and McColm's experience[8]. The measurements of specific refraction, which were also quoted in support of the polycyclic spiro structure by Staudinger and Geiger, seem definitely too low for a monocyclic formulation. However, the specific refraction of rubber and cyclized rubber needs further investigation; pending this, not too much reliance should be placed on structural conclusions based on present values. The measured refractive index and particularly the density of rubber have been yielding continuously lower figures as purer specimens were prepared. Recent values, shown in Table V, give poor agreement with the refractivity calculated from the theoretical atomic values of Vogel[35].

TABLE V

PHYSICAL PROPERTIES OF RUBBER AND VARIOUS CYCLIZED RUBBERS

Polymer	Sintering temp. (° C)	Density	Refractive index	Specific refraction	
				Found	Calcd.
Rubber	≪0	0.9025 (20° C) (*1*)	1.519 (20° C) (*54*)	0.336	0.331
Cyclized rubber from					
Acids on rubber[3]	100–105	0.980–1.016	—	—	—
BF_3 on synthetic polyisoprene[3]	?	0.96–98?	1.535	—	—
Zn + HCl on rubber halides[34]	110–130	0.992 (17° C)	1.5387 (17° C)	0.316	0.323
Heat on rubber[4]	—	0.992	—	—	—
H_2SO_4 on latex (this work)	95–110	0.992 (20° C)	1.5316 (20° C)	0.312	0.323

The refractive index of latex cyclized rubber shown in the table was found by first redispersing the wet flocculate with the aid of 0.25 per cent of sodium hydroxide (calculated on the polymer) and pebble-milling for 48 hours. A drop of the resulting dispersion, when deposited on the prism of an Abbé refractometer and spread out, left a uniform thin powdery deposit on drying. This was instantaneously fluxed to a transparent film by pouring over it carbon disulfide vapor from a bottle. After 3 days, it was assumed that the small amount of carbon disulfide had evaporated from the film, and the reading was taken as in the normal procedure used with a liquid. A sharp-edged shadow was obtained and the refractive index could be read to 0.0004 by several observers. The possibility of some solvent retention or oxidation of the film, however, cannot be excluded entirely by this method. The calculated specific refraction for cyclized rubber as shown is based on the statistical monocyclic product of 57 per cent unsaturation. In addition to the somewhat doubtful values of refractive indexes, Staudinger's supposed polycyclo products agree rather well in sintering temperature with both Fisher's and the writer's values for monocyclic polymer. This temperature, though naturally not sharply measurable, is remarkably sensitive to the degree of cyclization of latex cyclized rubber, so Staudinger's polymers are not likely to differ very greatly in cyclization degree from those of the other workers. Finally, the densities of Staudinger's supposed mono- and polycyclic rubbers were exactly identical with each other and with the writer's latex cyclized rubber and very nearly with Fisher's average figure. It is, therefore, proposed that cyclized rubber prepared by these various authors is a well defined monocyclic product.

Concerning the thermal cyclization of rubber, it may be speculated that this is an ionic reaction promoted by relatively weak acids derived from protein and other contaminants. The reaction proceeds[4] in a few hours at 300° to 320° C. It can be calculated, on the assumption of a constant activation energy of 33 kg.-cal. by a wide extrapolation, that an acidity of $H_0 = \text{pH} = +1$ is approximately sufficient to account for such rates.

SUMMARY

Kinetic measurements on rubber cyclization now are possible by a latex technique; these were undertaken to elucidate the mechanism of the reaction. According to a patented process, dispersions of Hevea latex particles in 70 to 80 per cent sulfuric acid are reproducibly isomerized to a high molecular weight cyclized rubber. A diffusion gradient technique was adopted for measuring the density of the polymer after exposing it to cyclization for varying times. Unimolecular constants, k, spreading over four decades, were obtained and found enormously sensitive to the percentage, c, of sulfuric acid and absolute temperature, T; thus $\log_{10}k = 6 + 0.17c - 7105/T$. The constants, k, correlate satisfactorily with Hammett's acidity function, H_0. A statistical theory by Flory shows that 13.5 per cent of the isoprene units originally present in rubber are left uncyclized by the reaction. This is in striking agreement with unsaturation measurements made by Fisher in 1927.

The kinetic parameters deduced support a nonchain proton transfer mechanism, deprotonation being rate-determining. The proton affinity of rubber is estimated, and a comparison of the cyclization of rubber and other terpenes is presented. The structure proposed for cyclized rubber rings by D'Ianni and co-workers is supported by mechanistic analysis and physical properties.

The method of kinetic measurements on stable emulsions in sulfuric acid is of general promise, and the cyclization of rubber polymer presents a useful model reaction for the smaller terpenes.

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THE STRUCTURE OF CYCLIZED RUBBER *

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INTRODUCTION

It is well known among rubber chemists that the preparation of rubber derivatives is often disturbed by a side reaction which leads to the formation of a hard and brittle resin of the same empirical composition as rubber[1]. This modification of rubber is assumed to be due to isomerization, which takes place especially under the influence of electrophilic agents[2] or heat[3], with the formation of internal rings, the process being accompanied by a loss of double bonds. This phenomenon is termed cyclization, and the products are referred to as cyclized or cyclorubbers[1].

In this paper a structural formula for cyclized rubber is proposed. In addition it is shown that the use of a more reliable method for the determination of the unsaturation of cyclized rubber is very helpful in the elucidation of its structure.

HISTORICAL

Harries[4] was the first author to describe the preparation of cyclized rubber, with sulfuric acid as a cyclizing agent. Other investigators, including Kirchhof[5], Staudinger[1], Fisher[6], studied the same reaction. Whereas the latter author introduced *p*-toluenesulfonic acid as a cyclizing agent, metal halides like $SnCl_4$, $TiCl_4$ and $FeCl_3$, and in general Friedel and Crafts catalysts, were used by Bruson, Sebrell, and Calvert[7].

Since 1930 a great many patents have been disclosed concerning the preparation of cyclized rubber, the common feature in practically all these methods being the use of acceptor molecules[2]. As the starting material, rubber in solid form or in solution is used. Recently the author discovered a new method for the manufacture of cyclized rubber, starting from natural rubber latex[8].

Cyclized rubber can also be made from rubber hydrochloride. Staudinger and his coworkers[9] were able to show that cyclized rubber is formed by the interaction of rubber hydrochloride and zinc chloride in toluene by prolonged heating. Also rubber hydrobromide and hydroiodide can be used as starting materials.

We shall now turn to the different formulas attributed to cyclized rubber by those authors who have concerned themselves with this polymer.

STRUCTURAL FORMULAS OF CYCLIZED RUBBER

So far the following formulas for cyclized rubber have been proposed (see Table I)[10].

The argument for such formulations in most cases is the fact that the determination of the unsaturation by means of iodine chloride shows a decrease in unsaturation in cyclized rubber compared with the starting material, rubber.

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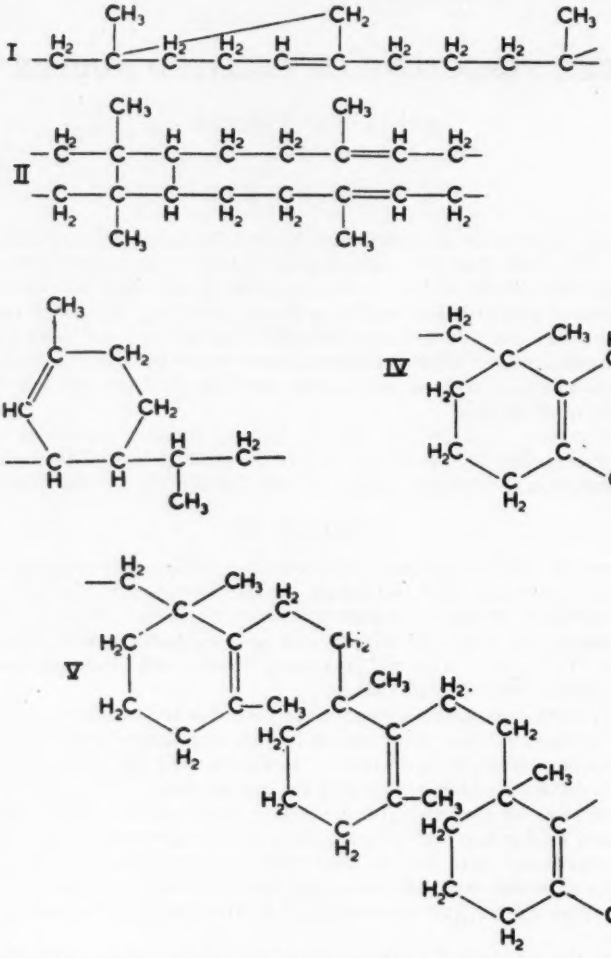
TABLE I



This method however is very unreliable[11], particularly in the case of cyclized rubber.

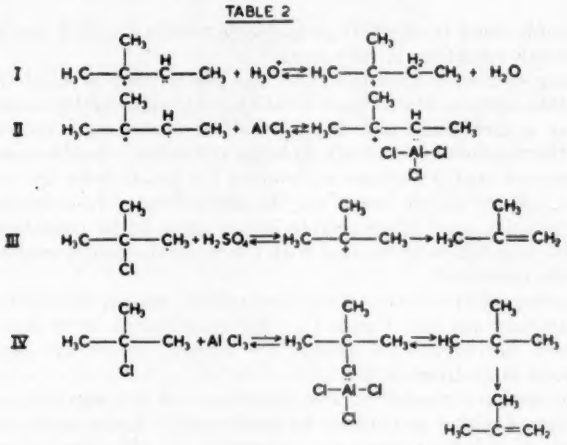
Formula IV corresponds to the structure which Tiemann[12] ascribed to the product obtained from the cyclization of geraniolene to cyclogeraniolene, with sulfuric acid as a catalyst. A similar formulation has been given by Bloomfield[13] to the product which is formed by the cyclization of dihydromyrcene with sulfuric acid-acetic acid. This author assumes that the reaction proceeds through a Whitmore mechanism[14], involving positive carbonium ions.

Before giving our formulation of cyclized rubber and our method for the determination of the unsaturation, we shall discuss briefly the mechanism of cyclization.

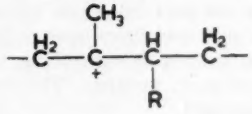
THE MECHANISM OF CYCLIZATION AND THE STRUCTURE OF CYCLIZED RUBBER

The acceptance of a Whitmore mechanism for the cyclization of geraniolene and dihydromyrcene means that cyclization of natural rubber is distinguished from true olefinic polymerization only by its purely intramolecular character[15]. We need not however, confine ourselves to reactions between olefins and sulfuric acid. Electronic theory enables us to describe the reaction between pronounced acceptor molecules on the one hand and rubber and rubber hydrochloride on the other hand from the same point of view. This may be illustrated by the following reaction schemes (Table II)[16].

TABLE 2



All these reactions are assumed to proceed through carbonium ion structures. If we return now to rubber and rubber hydrochloride and apply the same concepts as described above, then we may assume that in the first step (initiation), in the reaction of acceptor molecules with rubber and rubber hydrochloride, respectively, the same reaction intermediate occurs, namely:



in which R is H or $AlCl_3$, BF_3.

By analogy with what we know at present about ionic polymerization[17], we may assume that in the second stage of the reaction (propagation), the carbonium ion now formed acts as an acceptor, which reacts with the next double bond (Figure 1). Since the double bonds in rubber occur in 1,5-positions, it is reasonable to assume that adjacent double bonds react with each other. In this way, six-membered rings are formed, which are sterically most favorable. This is probably the main reason why cyclization is an intramolecular process, for which experimental evidence is given by the fact that no gelation takes place during the cyclization of rubber in solution. Apparently, the possibility of a

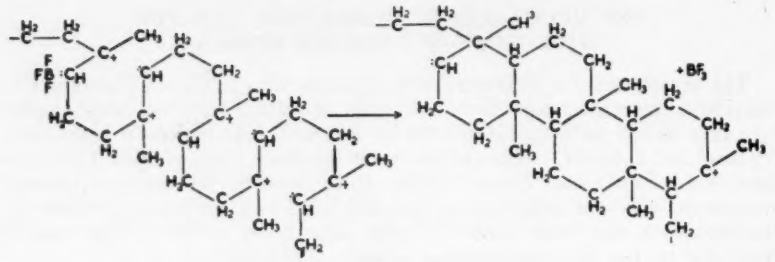


FIG. 1.

polarized double bond in one rubber molecule reacting with a double bond in another molecule of rubber is very small[18].

In the case of rubber hydrochloride, one has to bear in mind that, in the first step of this reaction, the tertiary C—Cl bond is loosened by complex formation, forming a carbonium ion structure which is the same intermediate as assumed in the reaction between alkyl olefins and acids. In the case of rubber, we have assumed that a tertiary carbonium ion reacts with the neighboring double bond. Since double bonds may be easily formed from tertiary halides through carbonium ions, these double bonds have to be considered here as intermediates, which is in agreement with the modern concept concerning Friedel and Crafts reactions.

To make clear the formation of cyclized rubber, we can formulate the intermediate in another way (see Figure 1). We assume that, from this intermediate, condensed polycycloheyxl groups are formed, which are probably the structural units in cyclized rubber.

Thus far we have considered the initiation and propagation of the ionic polymerization of rubber and rubber hydrochloride. As far as the termination reaction is concerned, the following may be said. If after the formation of, let us say, four cyclohexyl rings (Figure 1) the catalyst is removed, *e.g.*, by chain-transfer, then we observe that some irregularity occurs at the beginning and the end of the condensed polycyclohexyl group. At the left hand end we find an electron surplus, whereas at the right hand end an electron deficient carbon atom appears. In answering the question how such a structure may be stabilized, we refer to the termination reaction in the polymerization of isobutene with BF_3 as a catalyst[17]. In our particular case we assume that a double bond is formed somewhere in the polycyclohexyl group, for which evidence will be given. At this moment we cannot say anything about the location of the double bond in the polycyclohexyl groups. The results of further work on model substances must be awaited.

In summarizing, in our opinion cyclized rubber consists of condensed polycyclohexyl groups connected by shorter or longer polyisoprene chains.

From our mode of formulation it follows that at least two types of double bonds must occur in cyclized rubber:

(1) the polyisoprenic type of double bonds in the polyisoprene chains; (2) the double bonds in the condensed polycyclohexyl groups.

We will point to the fact that, in terpene chemistry, many compounds have analogous structures to those we ascribe to the polycyclohexyl groups in cyclized rubber. According to the iosprene rule of Ruzicka, terpenes, carotinoids

and probably sterols, hormones, bile acids, digitonides, and vitamins may be assumed to be built up from isoprene. Most of these compounds consist of six-membered rings or rings connected by short chains of polyisoprene or polyene and, in exceptional cases, of short chain molecules (squalene). As an example of a naturally occurring cyclized polyisoprene we mention here α-amyrin, the most probable structure of which is given here[19].

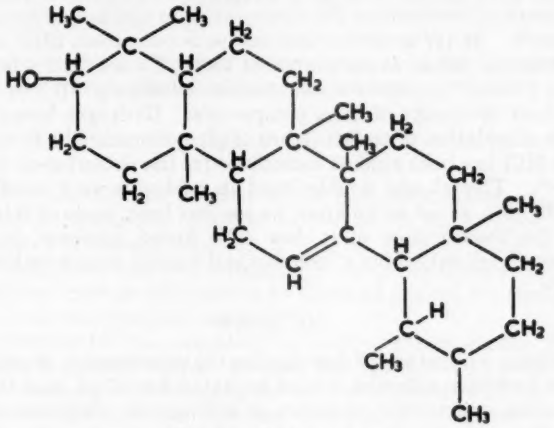


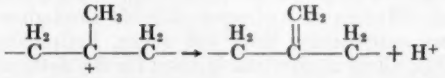
FIG. 2.

The similarity in carbon skeleton to that of cyclized rubber is very clear.

Another illustration of how our formulation of cyclized rubber fits well into the features of terpene chemistry is the cyclization of squalene[20].

Mention may be made also of the theory proposed by Tobolsky[21] and co-workers, in which the formation of cyclic terpenes and related compounds is assumed to proceed by an oxidative degradation of *trans*-polyisoprene.

We wish to emphasize that our formulation of the cyclization of rubber is a simplification of what will happen in reality. It is well known that olefins undergo isomerization and degradation under the influence of Friedel and Crafts catalysts. That in our case isomerization takes place during cyclization of rubber has been shown by means of infrared analysis of cyclized rubber, which gave evidence for the existence of $C{=}CH_2$ groups[22]. The occurrence of such types of double bonds may probably be explained by a stabilization of the carbonium ion structure:



DETERMINATION OF UNSATURATION IN CYCLIZED RUBBER

To give experimental evidence for our hypothesis concerning the structure of cyclized rubber, it was of prime necessity to determine the unsaturation. Detection of the two types of double bonds following logically from the derived structure of cyclized rubber was especially desired. Though bromine and iodine chloride are suitable reagents for the determination of the amount of

double bonds in rubber, these are absolutely useless in the case of cyclized rubber. Besides addition, considerable substitution takes place[23]. This phenomenon can readily be explained from our formula of cyclized rubber. It is known that tertiary hydrogen atoms are very easily substituted by halogens. The occurrence of tertiary hydrogen atoms in the structure of cyclized rubber proposed in this paper may be considered in connection with the high degree of substitution by halogens as an argument in favor of our formulation.

Other means of determining the unsaturation in cyclized rubber are found in the literature[24]. As far as hydrochlorination is concerned, little use has been made of hydrogen halide as an analytical tool. To mention a few examples. Nicolet and Poulter[25] applied the quantitative addition of HCl to the epoxides as a control on the purity of these compounds. Hydrogen bromide has been used for the elucidation of the structure of phenolformaldehyde resins[26]. The addition of HCl has been applied sometimes for the detection of double bonds in terpenes[27]. Though the double bond in rubber is very reactive towards hydrogen chloride, as far as we know no use has been made of this reaction to determine the unsaturation of rubber. We found, however, in the hydrochlorination of cyclized rubber a valuable and helpful means for the analysis of its structure.

METHODS

In describing our method of determining the unsaturation of cyclized rubber by means of hydrogen chloride, it must be stated first of all, that the method is time consuming and rather expensive in comparison with ordinary titration methods. Secondly, attention has to be paid to the fact that the use of HCl as an analytical tool with respect to unsaturation is still in its infancy. Since hydrochlorination of olefins is known to be a higher order reaction[28] and different types of olefins react quite differently with HCl, the method must be carefully applied. In our laboratory, experiments are underway to determine the reactivity of a series of olefins towards hydrogen chloride under different conditions. On the other hand, there are several facts in favor of the use of HCl. Thus far, hydrochlorination of rubber has led to products which contain 95 per cent of the theoretical value (33.9 per cent Cl) of the chlorine content, which was explained by some authors[29] by assuming that during hydrochlorination cyclization partly took place. The hydrochlorination of rubber in latex[30], however, has proved that 98 to 99 per cent of the theoretical chlorine content can be reached. From this the conclusion may be drawn that hydrochlorination of rubber in latex and probably in solution under normal conditions can be carried out without being disturbed by cyclization. Another advantage of the method is that insoluble polymers can be analyzed. Addition of hydrogen chloride to suitable solvents increases the swelling of rubber or cyclized rubber, which means that diffusion of hydrogen chloride throughout the polymer is guaranteed. Since substitution does not occur, hydrochlorination may be judged as a suitable, albeit a laborious method for the determination of the unsaturation in cyclized rubber.

For the detection of the two types of double bonds in cyclized rubber, the following two methods have been used.

(1) *Hydrochlorination under normal conditions.*—Half a gram of the polymer (rubber, cyclized rubber) is dissolved or swollen in 10 cc. of toluene. Instead of leading in HCl gas, which is inconvenient in the case of routine determinations, 50 cc. of a mixture of toluene and dioxane (2:1 vol.) saturated with HCl at

−50° C are added to the swollen polymer. After standing 24 hours at room temperature, the hydrochlorinated product is precipitated with alcohol and, after drying (in vacuo at 50° C), the chlorine content is determined by the Carius method.

(2) *Hydrochlorination under pressure.*—Hydrochlorination under pressure is carried out in the same way except that the reaction takes place in a sealed tube. The only difference from the method described under (1) is that a very high concentration of hydrogen chloride is present in the reaction mixture. The temperature in both cases is 20° C.

If the unsaturation of natural rubber is taken as 100, the unsaturation of cyclized rubber can be calculated from the formula:

$$\text{Uns.} = \frac{186.5\ X}{97.3 - X}$$

in which X is the chlorine content of the hydrochlorinated cyclized rubber. Since the hydrochlorination of rubber carried out in the way described affords products with a chlorine content of 31% ± 0.5 per cent (Uns. = 87) the unsaturation calculated from the theoretically correct formula will be a little too low. This disadvantage will have to be accepted against the straight-forwardness of the hydrochlorination reaction.

As a criterion for the complete hydrochlorination of the polyisoprenic double bonds in cyclized rubber, we used the fact that no increase in chlorine content was observed on prolonging the time of hydrochlorination (Method A). Since hydrochlorinated cyclized rubber (Method A), dissolved in chloroform, shows an intense yellow color with tetranitromethane (rubber hydrochloride containing 31 per cent Cl gives only a faint yellow color), information was gained that another type of double bond which is not hydrochlorinated under normal conditions (Method A) occurs in cyclized rubber. To detect this type of double bond more conclusively, drastic conditions of hydrochlorination (Method B) have to be applied. That this may be helpful in some cases has been shown by Salomon and Koningsberger[31]. Under normal conditions practically no hydrochlorination of the styrene-butadiene copolymer, GR-S, takes place. If pressure is applied during hydrochlorination, the internal double bonds in GR-S react readily with hydrogen chloride.

Before giving the results, it must be pointed out that the application of pressure might be dangerous since undesirable side reactions might take place. To control this the following experiments have been carried out. Rubber, rubber hydrochloride and cyclized rubber were treated with hydrogen chloride (Method B) at 100° C. By carrying out these experiments in a series of sealed tubes, the chlorine content could be determined at different times. The results are shown in Table III and graphically presented in Figure 3.

TABLE III

TREATMENT OF RUBBER, RUBBER HYDROCHLORIDE AND CYCLIZED RUBBER WITH HYDROGEN CHLORIDE (METHOD B) AT 100° C

Time in hrs.	Rubber		Rubber hydrochloride		Cyclized rubber unsat.: 43 (Method B)	
	% Cl	Unsat.	% Cl	Unsat.	% Cl	Unsat.
4	28.2	77	29.7	82	15.0	34
72	12.3	27	12.8	28	9.8	21
96	10.3	22	12.0	26	9.0	19
209			9.0	19	7.3	15

The results show that, under the conditions used, rubber and cyclized rubber are hydrochlorinated rapidly and that on prolonged time of reaction the chlorine content and the unsaturation calculated from the chlorine contents decrease, which means that cyclization has taken place.

Rubber hydrochloride shows the same phenomenon. The unsaturation of rubber hydrochloride plotted in Figure 3 against time is to be considered as the unsaturation of rubber, from which it is prepared.

From these experiments it appears that our assumption that hydrochlorination of rubber is not accompanied by cyclization holds only as far as special conditions are concerned. At higher temperatures and pressures, hydrogen chloride acts as a cyclizing agent as well as hydrogen fluoride under normal conditions.

The same experiments repeated at 50° and 20° C showed that neither decrease nor increase in chlorine content takes place if the time of reaction is

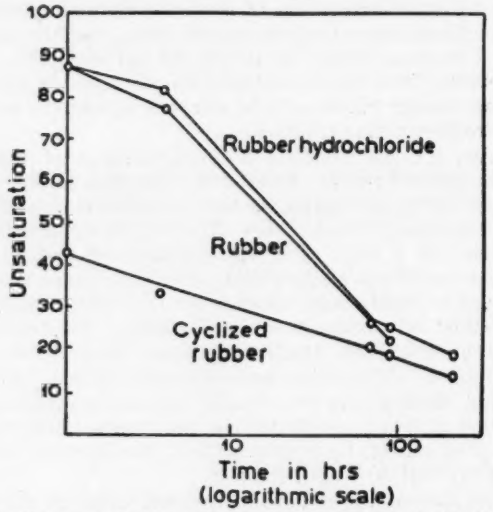


FIG. 3.—Treatment of rubber, cyclized rubber and rubber hydrochloride, with hydrogen chloride under pressure (Method B) at 100° C.

sufficiently long. In addition, practically no double bonds could be detected in these hydrochlorinated polymers by means of tetranitromethane. Our conclusion is, therefore, that Method B leads to practically fully hydrochlorinated cyclized rubber.

As far as the reproducibility of the two methods of hydrochlorination is concerned, the results of experiments with fifteen samples of cyclized rubber in which the hydrochlorination and chlorine analysis were carried out in duplicate showed that in the region of most frequently occurring chlorine contents (9 to 19 per cent), the average deviation is ±0.5 per cent.

RESULTS

A great many samples of cyclized rubber have been hydrochlorinated by the two methods. A few examples may show the difference in chlorine content obtained by using the two methods (Table IV).

TABLE IV

CYCLIZED RUBBER HYDROCHLORINATED UNDER NORMAL CONDITIONS (METHOD A, 1 ATM. 20° C) AND UNDER PRESSURE (METHOD B SEALED TUBES 20° C)

Sample no.	Method A		Method B		Difference	
	% Cl	Unsat.	% Cl	Unsat.	% Cl	Unsat.
1	8.4	18	10.5	23	2.1	5
2	5.3	11	8.1	17	2.8	6
3	23.9	61	26.2	69	2.3	8
4	13.5	30	19.0	45	5.5	15
5	9.9	21	14.8	33	4.9	12
6	9.3	20	15.1	34	5.8	14
7	8.1	17	12.9	28	4.8	11

Description of the samples.

Samples 1 and 2 were cyclized rubbers prepared from rubber in benzene solution using $SnCl_4$ as a catalyst. Temperature 65° C and time of reaction 80 and 145 minutes, respectively.

Samples 3–7 were cyclized rubbers prepared from latex.

Table IV clearly shows that a difference in chlorine content and, therefore, in unsaturation exists from using the two methods of hydrochlorination. This difference is relatively small in the case of cyclized rubbers prepared from solution and amounts to about 5 per cent Cl in cyclized rubber prepared from latex. If the degree of cyclization is small (Sample 3), the difference in chlorine content decreases, which is quite natural in view of our working hypothesis.

Our experiments indicate that at least two types of double bonds occur in cyclized rubber. The double bonds hydrochlorinated under normal conditions belong to the polyisoprenic type, whereas the double bonds with a lower reactivity towards hydrogen chloride are located in the polycyclohexyl groups. The polyisoprenic unsaturation is determined by Method A, whereas the polyisoprenic and polycyclohexylic or total unsaturation is found by Method B. Furthermore we refer again to the results of infrared analysis, which showed that double bonds of the type $C{=}CH_2$ are also present. Quantitative data are not available. We presume, however, that only a minor part of the polyisoprenic double bonds have isomerized to this type. Since this type of double bond can be hydrochlorinated easily[32], it will probably behave as an ordinary polyisoprenic double bond. Therefore no trouble may be expected from the occurrence of this type of double bond as far as our analysis of the structure of cyclized rubber is concerned.

The occurrence of different types of C—Cl bonds in fully hydrochlorinated cyclized rubber can in principle be demonstrated by kinetic analysis[33]. In preliminary experiments we have encountered difficulties caused by the insolubility of the hydrochlorinated cyclized rubber in aniline. Further experiments will have to be carried out.

THE DETERMINATION OF THE RATE OF REACTION AND THE INFLUENCE OF SOLVENTS ON THE CYCLIZATION OF RUBBER

To illustrate the continuous character of the cyclization reaction, which makes the older distinction between mono- and polycyclorubber meaningless[9], and the influence of solvents, we shall describe the following experiments in which Method A was used for hydrochlorination. To a solution of rubber in toluene (5 volume-per cent) 3.5 percent by weight of sulfuric acid calculated on rubber was added. The rate of reaction was determined at different tem-

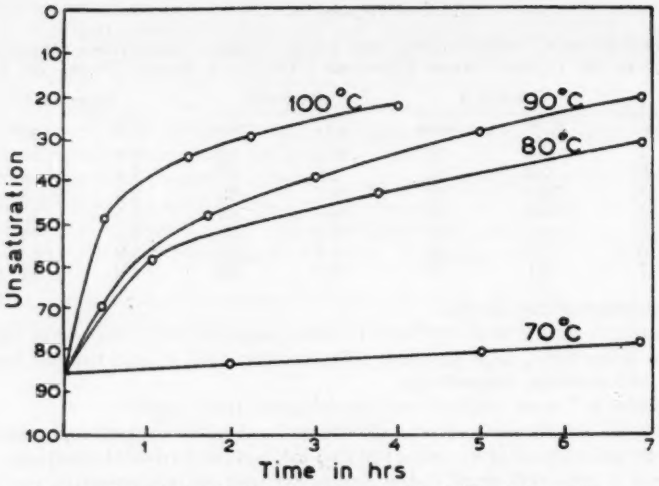


FIG. 4.—The rate of cyclization of rubber in solution at different temperatures.

peratures, namely, 70, 80, 90 and 100° C. During the reaction, samples were extracted and the polyisoprenic unsaturation was determined.

The polyisoprenic unsaturation values were taken as a measure of the degree of cyclization. The curves which denote the rate of reaction are given in Figure 4.

Figure 4 shows the effect of temperature on the rate of cyclization. At 70° C the reaction scarcely takes place. At 80, 90 and 100° C the rate of reaction is considerable. In the last three cases especially, the initial rate is high, whereas with increasing time the rate rapidly decreases, which is in agreement with the acceptance of an ionic polymerization reaction scheme.

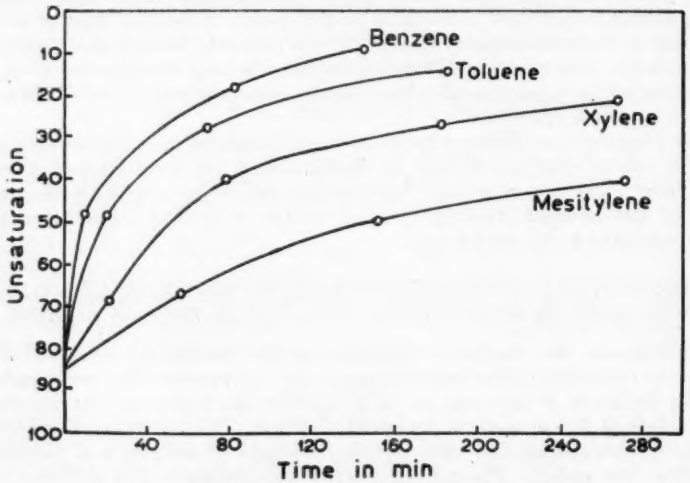


FIG. 5.—The influence of solvents on the rate of cyclization.

Another advantage of our method for the determination of the unsaturation in cyclized rubber is that it enables us to investigate the influence of solvents on the cyclization reaction. For this purpose the rate of cyclization was determined by heating 5 per cent solutions of rubber in benzene, toluene, xylene, and mesitylene, respectively, with 12 per cent of stannic chloride (calculated on rubber) at 65° C. The polyisoprenic unsaturation of samples of cyclized rubber withdrawn during the reactions was determined in the way described and taken as a measure of the degree of cyclization. The results are shown in Figure 5.

The results show that the rate of reaction decreases in the series benzene, toluene, xylene, and mesitylene, which may be explained by the fact that the increasing donor properties of these solvent molecules impede more and more the catalytic effect of the acceptor molecule $SnCl_4$, by a greater tendency to form complexes with this Friedel-Crafts catalyst. This solvent effect may be seen in the same light as the gradual shift in color of iodine in this series of solvents[34] from red-violet to brown and the increasing reactivity of these molecules towards ozone[33].

DISCUSSION

The formulations suggested in this paper explain several chemical properties of cyclized rubber. The decrease in unsaturation during cyclization is in agreement with the acceptance of an ionic polymerization scheme. The results of our experiments have shown that at least two types of double bonds occur in cyclized rubber, and this agrees with the structure proposed. We have suggested that the double bonds which react with hydrogen chloride under normal conditions belong to the polyisoprenic type and that the double bonds reacting only under pressure are located in the polycylcohexyl groups. With respect to the low reactivity of part of the double bonds, a feature well known in terpene chemistry may be mentioned. Ruzicka has shown in several cases that cyclic terpenes like α-amyrin contain a souble bond which can be hydrogenated only under pressure. The existence of these double bonds, which do not react with peroxyacids, can be detected by means of tetranitromethane. Ruzicka[19] ascribes the low reactivity of the double bond in α-amyrin to the fact that a methyl group has a screening effect on the neighboring double bond. Possibly the same explanation has to be assumed in cyclized rubber.

The occurrence of tertiary hydrogen atoms in our formulation for cyclized rubber may explain the unreliability of iodine chloride and bromine as a means for the determination of the unsaturation. Furthermore, the oxidizability of cyclized rubber[2] must probably be ascribed to the same fact.

It will now be shown that the structure ascribed in this paper to cyclized rubber also readily explains some physical and mechanical properties of isomerized rubber. If rubber is converted into cyclized rubber, the density and refractive index increase. In low molecular chemistry it is well known that conversion of a linear olefinic molecule to the corresponding cyclic molecule is accompanied by an increase in density, whereas in terpene chemistry the increase in refractive index on cyclization of linear terpenes is a well established fact.

As far as the mechanical properties are concerned, we may mention the gradual increase in brittle point in passing from raw rubber to cyclized rubber. Rubber becomes brittle at $-59°$ C, whereas cyclized rubber (polyisoprenic unsaturation about 30) is brittle at room temperature and has its weakening point at 70 to 90° C. The formation of condensed polycyclohexyl groups in the flexible rubber molecules immobilize these parts of the long rubber chain.

On increase of the amount of polycyclohexyl groups, the material becomes hard. In fact, when the ratio of polycyclohexyl groups to polyisoprene chains is high enough, a brittle resin is obtained. In this respect we may point to the properties of rosin, containing about 90 per cent of abietic acid, which is similar in structure to the condensed polycyclohexyl groups in cyclized rubber.

Finally, it may be mentioned here that the investigation of the structure of cyclic pentenes as carried out, *e.g.*, by Ruzicka and his coworkers, is very difficult, notwithstanding the fact that melting points and specific rotations of these compounds can be determined, and one compound can be interrelated with another by chemical modification, all of which is impossible in the case of cyclized rubber.

A more detailed elucidation of the structure of cyclized rubber, which is now brought into line with our knowledge of low molecular terpene chemistry, will have to await further progress in this field.

SUMMARY

The history of cyclized rubber, including a series of structural formulas previously proposed for this polymer, is reviewed briefly.

A new formula for cyclized rubber is suggested by applying electronic interpretations of reactions between electrophilic agents and tertiary alkyl olefins and tertiary halides, respectively, to the corresponding reactions with rubber and rubber halides.

It is shown that hydrochlorination can be used for the determination of the unsaturation of cyclized rubber. By varying the conditions of hydrochlorination, two types of double bonds can be detected in cyclized rubber, a fact which is in agreement with the structure suggested.

By using our method for the determination of the unsaturation, the rate of cyclization at different temperatures and the influence of solvents on the rate of reaction have been determined.

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CHLORINATION OF NATURAL AND SYNTHETIC POLYISOPRENES*

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INTRODUCTION

Since natural rubber was first chlorinated in 1859[1], a large amount of work has been directed toward elucidation of the mechanism of the chlorination[2]. While the early work in this field correctly established that the chlorination of rubber involves both substitution and addition, the recent classical work of Bloomfield[3] has provided a basic understanding of the various reactions involved.

In view of the considerable interest in synthetic polymers, it seemed of interest to study in detail the chlorination of synthetic polyisoprene and to compare that elastomer with Hevea (*cis*) natural polyisoprene and gutta-percha (*trans*) natural polyisoprene. Synthetic polyisoprene contains both *cis* and *trans* internal double bonds and, in addition, differs from the natural polyisoprenes in that approximately 10 per cent of the double bonds are in vinyl side chains resulting from 1–2 rather than 1–4 addition of monomer units during polymerization. D'Ianni and coworkers[4] have reported a close similarity in the properties of chlorinated synthetic polyisoprene and chlorinated Hevea rubber.

PRESENT INVESTIGATION

Using a refinement of the chlorination technique of Bloomfield[3], the substitutive and additive reactions of chlorine with emulsion polyisoprene, Hevea and gutta-percha were followed quantitatively. Results are summarized graphically in Figures 1–4, in which the curves numbered 1 represent the number of chlorine atoms per isoprene unit in the chlorinated polymers as a function of the number of Cl_2 molecules reacted per isoprene unit. Curves 2 and 3 represent the substitutive and additive chlorine atoms, respectively, also as a function of total Cl_2 molecules reacted per isoprene unit.

Figure 1 essentially confirms the results of Bloomfield[3], and in addition indicates that *trans* gutta-percha is quite similar to *cis* Hevea. The chlorination proceeds in three stages, (1) the first molecule of chlorine reacting leads almost exclusively to substitution; (2) the next 1.2 molecules of chlorine react by both substitution and addition, and (3) when approximately 2.2 molecules of chlorine per isoprene unit have reacted, the additive reaction ceases abruptly and all further reaction occurs by substitution. Under the mild conditions employed, reaction ceases when the chlorine content of the polymer is approximately 64 per cent, corresponding to about 3.38 atoms of chlorine per isoprene unit. Our results at 30° show that at this point a total of 2.81 moles of Cl_2

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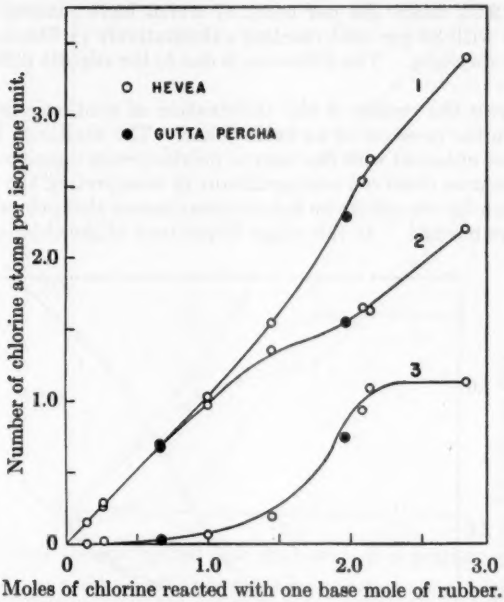


FIG. 1.—Addition and substitution in the chlorination of Hevea and gutta-percha at 30° and in the presence of an antioxidant: 1, total chlorine; 2, substitutive; 3, additive.

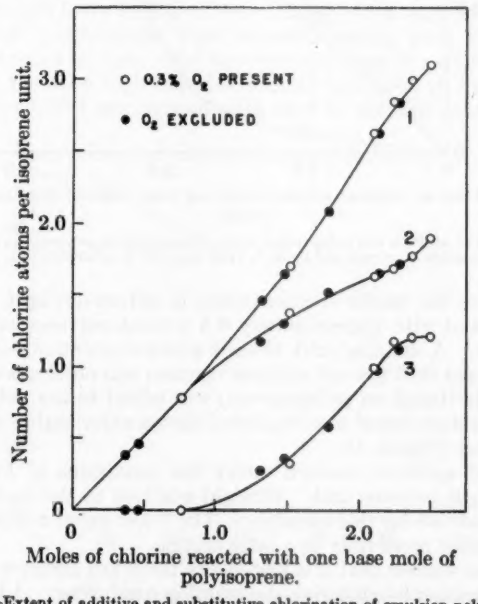


FIG. 2.—Extent of additive and substitutive chlorination of emulsion polyisoprene in darkness: 1, total chlorine; 2, substitutive; 3, additive.

have reacted, 2.24 moles (80 per cent) of which have reacted sustitutively. This compares with 84 per cent reacting substitutively in Bloomfield's experiments at 77° in daylight. The difference is due to the slightly different reaction conditions.

Figure 2 gives the results of the chlorination of synthetic polyisoprene in darkness and in the presence of an antioxidant. The similarity between these results and those obtained with the natural polyisoprenes is marked. However, the slight differences observed are significant in interpreting the results. The additive reaction for the synthetic polyisoprene ceases abruptly when 2.3 moles of chlorine have reacted. At this stage 75 per cent of the chlorine has reacted substitutively.

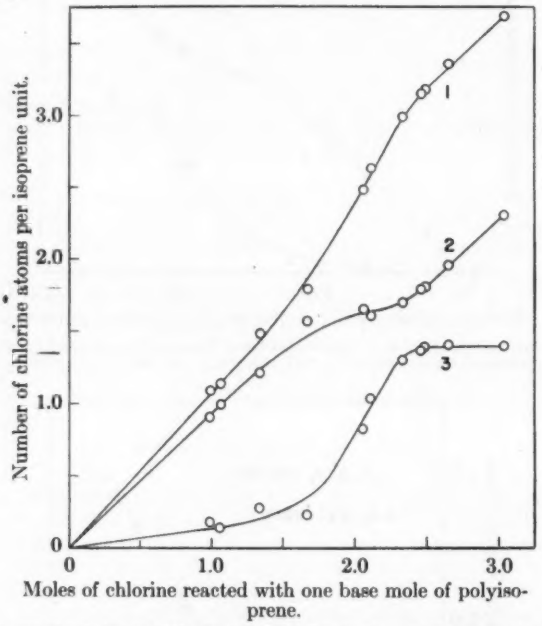


FIG. 3.—Extent of addition and substitution in the chlorination of polyisoprene in the presence of small amounts of oxygen and light: 1, total chlorine; 2, substitutive; 3, additive.

Figure 3 gives the results of chlorination in diffuse daylight, in the absence of antioxidant and with approximately 0.3 volume per cent of oxygen in the chlorine stream. A definite shift toward additive reaction can be observed. A very pronounced shift toward additive reaction was obtained when 1 per cent benzoyl peroxide (based on polyisoprene) was added to the polyisoprene solution, and the reaction vessel was irradiated during chlorination with a 100-watt mercury arc lamp (Figure 4).

The limit of additive reaction under the conditions of Figure 2 is 1.21 chlorine atoms per isoprene unit. Straight addition to the double bond would require a value of two for this quantity. The lower value is due to cyclization, as will be discussed more fully in a later section.

Figures 3 and 4 show that it is possible to favor the additive reaction at the expense of cyclization by changing the reaction conditions. Additional experi-

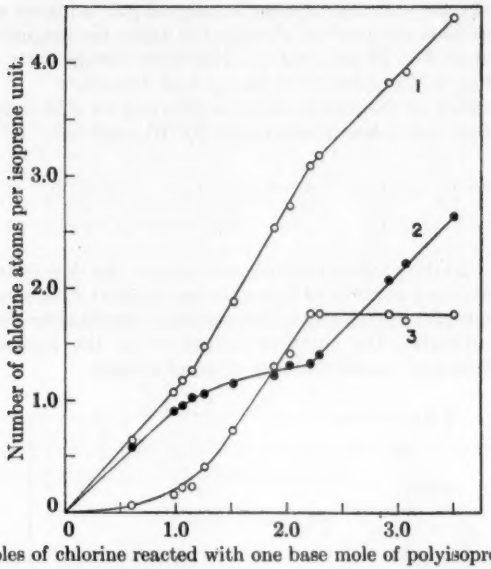


FIG. 4.—Extent of addition and substitution in the peroxide plus ultraviolet-catalyzed chlorination of polyisoprene: 1, total chlorine; 2, substitutive; 3, additive.

ments on the separate effects of benzoyl peroxide and light showed that peroxide alone does not favor addition, even though it strongly catalyzes the substitutive reaction. Ultraviolet light causes a strong shift toward addition. Only in the presence of both light and peroxide was it possible to carry the chlorination to the very high chlorine content indicated in Figure 4. (Final polymer contained 70.4 per cent chlorine or 4.39 chlorine atoms per isoprene unit.)

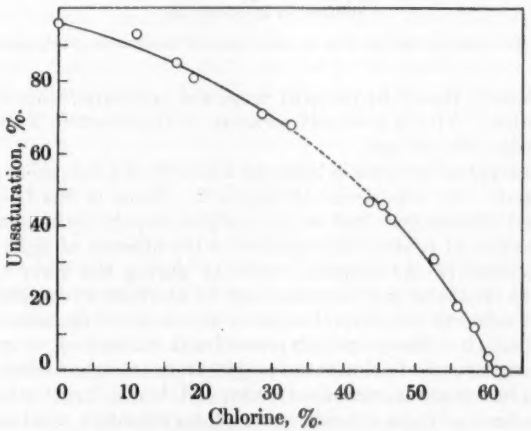
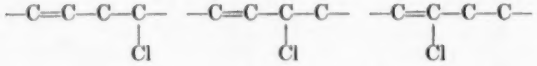


FIG. 5.—Unsaturation of chlorinated polyisoprenes.

Figure 5 shows the decrease in unsaturation of polyisoprene as a function of the per cent chlorine in the product chlorinated under the conditions of Figure 2. Values in the range 0 to 30 per cent chlorine were obtained by iodine chloride titration according to the method of Kemp and Mueller[5].

The applicability of the iodine chloride titration to chlorinated olefins and chlorinated rubber has been investigated by Bloomfield[6]. Of the following groups:



only the last one inhibits iodine chloride addition to the double bond. Since in the case of chlorinated rubbers of low chlorine content (not more than one Cl atom per isoprene unit) practically all the substitutive chlorine is removable with alcoholic silver nitrate[6], the chlorine cannot be in the 2-position[7], and the iodine value should give a true measure of unsaturation.

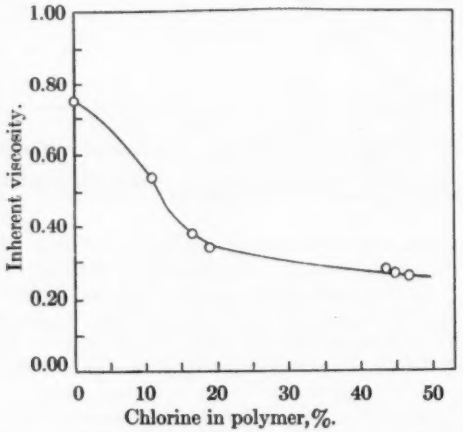


FIG. 6.—Inherent viscosity drop in early stages of chlorination of polyisoprene.

Unsaturation in the 42–64 per cent range was calculated from the remaining additive chlorine. This is a correct measure of unsaturation if the cyclization is complete below 40 per cent.

Figure 6 shows the decrease in inherent viscosity of a sample of polyisoprene chlorinated under the conditions of Figure 2. Since it has been shown by Staudinger and Staudinger[8] that no appreciable depolymerization takes place in the chlorination of rubber hydrocarbon in the absence of light and oxygen, the rapid decrease in the inherent viscosity during the early stages of the chlorination of synthetic polyisoprene may be ascribed to cyclization. While it is true that inherent viscosity changes of this order of magnitude might also be effected through a change in polymer-solvent interaction, it appears to the authors that, in the case of chlorinated polyisoprene in carbon tetrachloride, this change would be toward increased solvation and, hence, larger inherent viscosities. On the basis of these considerations, the cyclization reaction appears to be essentially complete below 40 per cent chlorine.

DISCUSSION

Examination of Figure 2 indicates that the total amount of chlorine which can be added to the double bonds is only somewhat more than half of the amount that could be expected to add on the basis of the initial unsaturation of the polyisoprene chlorinated. Since fully chlorinated polyisoprene contains no double bonds[4], about half of the initial unsaturation is lost by cyclization. If the cyclization is visualized as involving the formation of six-membered rings, the possibility of a reaction by pairs is suggested. One of the principal features of this type of reaction is the isolation of reactive units between reacted pairs. The possibility of isolation of reactive units was first recognized by Flory, who developed a statistical treatment for calculating the number of such units[9]. Applying the statistics of reactions by pairs to the cyclization of polyisoprene or rubber, one obtains for the fraction of isoprene units incapable of undergoing cyclization:

$$\frac{1}{n}\sum_{s=0}^{n-1}(-2)^s(n-s)/s! \qquad (1)$$

where n is the number of consecutive isoprene units in the chain. For chains of more than eight isoprene units, this reduces to

$$0.1353(1+2/n) \qquad (2)$$

to a close degree of approximation.

For long, uninterrupted chains of isoprene units, such as can be expected to occur in natural rubber, the fraction of uncyclized units would be approximately 0.135. Hence the theoretical limit of additive chlorine would be 1.135 atoms per isoprene unit. The value found (Figure 1) was 1.14. It is significant in this connection that the unsaturation of completely cyclized rubber (Thermoprene-SL)[10] is 57 per cent in excellent agreement with Equation (1).

In the example of synthetic polyisoprene, the problem is more complicated. Polyisoprene prepared by emulsion polymerization contains approximately 10 per cent external double bonds due to 1,2- and (or) 3,4-addition during polymerization. These cannot be expected to undergo cyclization in the same manner as the normal 1,4-isoprene units. Further, the total unsaturation of emulsion polyisoprene is slightly less than the theoretical. Assuming that these side chains and saturated units are lost to cyclization, it is still possible to estimate the total amount of additive chlorine. For polyisoprene of 96 per cent unsaturation and containing 10 per cent external double bonds we shall consider the spacing of the 1,2-addition units and the saturated units as entirely random. We shall further assume that only unsaturated 1,4-units are capable of undergoing cyclization. The statistical problem is then the same as in the removal of chlorine from copolymers of vinyl chloride, a case which has been treated by Wall[11]. The fraction of isolated units is given by Wall's calculation as e^{-2x}. In our example $x = 0.86$, so the fraction of isoprene units isolated is 0.179. The total amount of chlorine necessary to saturate all cyclized units, isolated units, and external double bonds is then readily calculated as 1.22 chlorine atoms per isoprene unit. The experimental value is 1.21 (Figure 2).

The sharp inherent viscosity drop observed in the early stages of the polyisoprene chlorination (Figure 6) suggests that cyclization precedes the additive reaction, a condition tacitly assumed in the statistical discussion. This is further borne out by the unsaturation of the low chlorine polymers as shown in

Figure 5. The amount of cyclization as calculated from unsaturation in the early stages of the chlorination is given in Table I.

TABLE I

CYCLIZATION IN THE EARLY STAGES OF CHLORINATION OF SYNTHETIC POLYISOPRENE AS DETERMINED BY IODINE CHLORIDE TITRATION

% Cl in polymer	% Unsaturated by I-Cl	Cyclization, double bonds lost/ isoprene unit*	Substitutive Cl per isoprene unit	Ratio substituted Cl to cyclization
0.0	96	0.00	0.00	—
16.6	85	.11	.38	3.4
19.0	81	.15	.46	3.1
28.6	71	.27	.77	2.9
32.6	68	.29	.89	3.1

* Theoretical limit is 0.36.

The last column of Table I indicates that, during the early stages of chlorination, there are approximately three chlorine atoms substituted for each double bond lost through cyclization, *i.e.*, the cyclization reaction appears to be brought about by the third chlorine molecule reacting with a particular isoprene unit. Alternatively, cyclization may be induced by the first (or second) chlorine molecule reacting, followed by rapid substitution of two (or one) more chlorines in the cyclized unit.

One of the essential features of the statistical treatment of the cyclization reaction is that there can be no appreciable addition of chlorine to double bonds other than those occurring in already cyclized units (or vinyl side chains) until all the cyclization is complete. After this, the isolated units add chlorine. The data support this hypothesis. At 36.2 per cent chlorine the degree of cyclization is 0.29, but additive chlorine is only 0.02 (probably resulting from addition to cyclized units). In the presence of light and peroxide the additive chlorine is much greater (Figure 4). Under these conditions, addition can apparently occur before cyclization, thus increasing the number of isolated units and decreasing the ultimate degree of cyclization. Thus, the total ultimate additive chlorine would be higher at the expense of cyclization. This is in agreement with experiment as shown by Figure 4.

EXPERIMENTAL

Method.—The apparatus is shown diagrammatically in Figure 7. A slow stream of chlorine (12–20 cc. per min.) and nitrogen in approximately equal proportions was introduced just below the surface of an agitated, dilute (20 grams per liter) solution of the purified polymer in reagent grade carbon tetrachloride. The evolved gases were passed through the condenser (C) and up the column (B) packed with metallic antimony and glass wool. Any chlorine escaping from the solution was removed by the antimony while the hydrogen chloride passed through the column into a 2 *N* sodium hydroxide solution in the trap (A).

Special tests showed that separation of chlorine and hydrogen chloride by the above method was quantitative provided that the antimony was first saturated with anhydrous hydrogen chloride. Consequently, the antimony used was first treated with anhydrous HCl and then blown free of adsorbed hydrogen chloride by a stream of dry nitrogen. As a precaution the standard alkali in the trap was checked for hypochlorite and antimony (from hydrolysis

of $SbCl_5$ vapors possibly carried into the trap) after each run. Both tests were consistently negative.

Commercial chlorine was used in all chlorinations. The gas was scrubbed with concentrated sulfuric acid (N) and liquefied in a dry-ice trap (L). Half of the liquid chlorine was distilled off and trapped in alkali (P). The residue, substantially free of oxygen and hydrogen chloride, was allowed to distill into the reaction flask (G). The switch from trap (P) to reactor (G) was accomplished

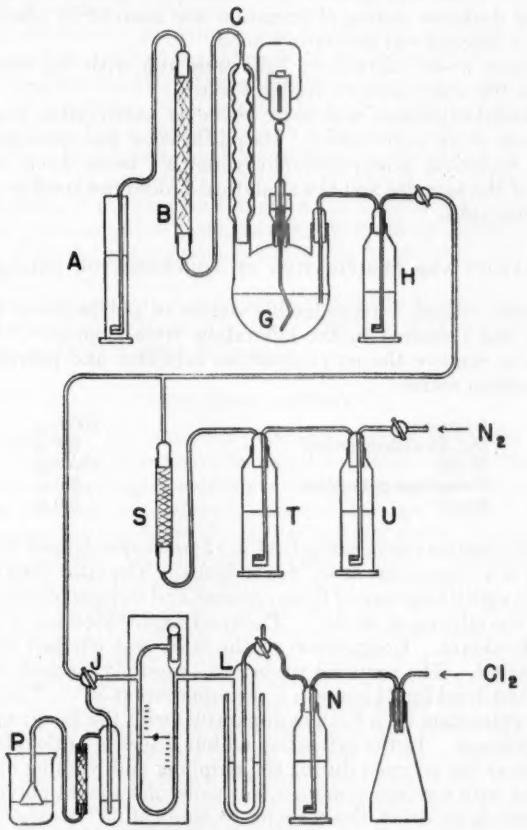


FIG. 7.—Apparatus for controlled chlorination of polymers.

simply by turning the three-way stopcock (J). In experiments in which total exclusion of oxygen was not desired, the distillation of the chlorine was omitted.

The purpose of using nitrogen as a diluent was two-fold. Nitrogen provides a neutral atmosphere and keeps the solution in trap (A) from sucking back into the system upon absorption of HCl. At the same time, secondary addition of HCl to the rubber molecule is prevented by the flushing action of the nitrogen[3]. Oxygen was removed from the nitrogen by passing the latter through a dilute solution of chromous sulfate[12] (U). The gas was then scrubbed with concen-

trated sulfuric acid (T) and passed through a phosphorus pentoxide drying tube (S) before being mixed with the chlorine. Again, in experiments not necessitating the strict absence of oxygen, the procedure was simplified by omitting the chromous sulfate bubbler. The nitrogen used contained 0.3 per cent oxygen by volume.

Before starting each chlorination, the entire system was blown out with nitrogen for at least 10 hours. Likewise, the nitrogen flow was continued after chlorination until the exit gases tested entirely neutral toward moist litmus paper. Total darkness during chlorination was insured by placing the entire apparatus in a blacked out laboratory hood.

Chlorinations under ultraviolet light were run with the reactor flask irradiated by a 100-watt mercury arc light source.

Phenyl-β-naphthylamine was used whenever chlorination was carried out in the presence of an antioxidant. Its purification was accomplished by recrystallizing technical phenyl-β-naphthylamine[13] twice from alcohol. The preparation of the samples and the analytical procedures used are given in the following paragraphs.

PREPARATION AND PURIFICATION OF POLYMERS FOR CHLORINATION

Polyisoprene.—Since a reproducible source of polyisoprene was required, polyisoprene was prepared in the laboratory from isoprene[14]. The isoprene was distilled to remove the polymerization inhibitor and polymerized in the following emulsion recipe:

Isoprene	100.0 g.
tert.-Hexadecanethiol	0.5 g.
Water	180.0 g.
Potassium persulfate	0.3 g.
Soap[15]	5.0 g.

The polymerizations were carried out in 12-oz. crown-capped bottles, rotated end over end in a thermostat at 50° for 30 hours. The latex thus obtained was short-stopped with 0.06 grams of hydroquinone and stripped of unreacted monomer by vigorous stirring at 50–60°. Phenyl-β-naphthylamine (1.2 grams) was added as antioxidant. Coagulation of the latex was effected by addition of 100 cc. of ethanol. The resulting rubber was carefully washed free of soap in warm water and dried for 24 hours in a vacuum oven at 50°. This was followed by a 24-hour extraction (in a Soxhlet apparatus) with the azeotropic mixture of ethanol and toluene. In the extraction all but traces of antioxidant originally added to protect the polymer during the stripping and washing operations was removed along with residual monomer, low molecular weight polymer and soap. The rubber was again dried, this time for 48 hours at 35° *in vacuo*. The resulting polyisoprene hydrocarbon was a colorless transparent soft polymer of nearly theoretical iodine value. It was stored in darkness in an evacuated desiccator.

Hevea.—Pale crepe was purified by a method similar to that described by Kemp and Peters[16]. Fifty grams of crepe was placed in a cloth bag and submerged in 1500 cc. of chloroform to which 0.2 gram of phenyl-β-naphthylamine had been added. Diffusion of the rubber into the solvent was allowed to take place for five days, after which the rubber was precipitated with methanol and redissolved in benzene. The benzene solution was then fractionally precipitated with a 50-50 mixture of ethanol and benzene and the first fraction discorded. According to Pummerer and Koch[17] all impurities are removed with

the first fraction. The rubber hydrocarbon was dried for 48 hours at 35° in a vacuum. Iodine chloride titration gave an iodine value of 370 for the final product (99 per cent of theoretical).

Gutta-percha.—Crude gutta-percha was dissolved in benzene and the solution filtered to remove grit and sand. The polymer was then precipitated with alcohol and extracted with the azeotropic mixture of ethanol and toluene. After two more precipitations, the product was dried in the manner described for polyisoprene and Hevea. The purified material had an iodine value of 364 (97 per cent of theoretical).

Isolation of chlorination products.—The chlorinated polymers were isolated from the CCl_4 solution by dropping the solution into boiling water to flash off the solvent. The product was then divided into small pieces and washed in boiling tap water for 30 minutes. This was followed by a similar wash in distilled water. The polymer was carefully dried in a vacuum oven at 50°.

The drastic treatment to remove the solvent is absolutely essential, since chlorinated rubbers are particularly apt to retain traces of solvents[18]. It was realized that boiling of the polymers might cause hydrogen chloride to be split off. However, in all but a few cases, no chloride could be detected in the wash water. Even when the water gave a positive test for chloride, the amount was quite negligible.

It was found convenient to precipitate polymers of low chlorine content with ethanol before boiling them in water. This was done merely to facilitate handling of the inherently sticky polymers.

ANALYTICAL METHODS

Chlorine analyses.—The pure dry polymers were analyzed for chlorine by sodium peroxide fusion (Parr bomb technique), followed by Volhard titration.

The amount of hydrogen chloride evolved during the chlorination was determined by titration of an aliquot from the standard alkali. The Volhard chloride determination was favored over back-titration with standard acid as a matter of convenience. No difficulty was encountered from traces of carbon tetrachloride swept into the alkali trap during chlorination.

Iodine chloride titrations.—The limitations of the iodine chloride titration have been discussed. The method of Kemp and Mueller[5] was applied successfully without modifications to polyisoprene, rubber and gutta-percha. However, with chlorinated polymers the procedure had to be modified to insure complete iodine chloride addition. The reason for this is two-fold: (1) the reaction is considerably slower for the chlorinated polymers, and (2) the low solubility of some of the chlorinated polymers further retards iodine chloride addition and leads to erratic results, as the titration must be carried out with a gel containing sample. These difficulties were largely overcome by allowing additional time for the iodine chloride addition to take place.

SUMMARY

The extent of additive and substitutive chlorination was determined for emulsion polyisoprene, Hevea and gutta-percha chlorinated to different chlorine contents in darkness and in a nitrogen atmosphere.

The maximum amount of additive chlorine that can be introduced into the polymer is 1.21 atoms of chlorine per isoprene unit for synthetic emulsion polyisoprene, 1.14 for Hevea. The chlorination involves a cyclization reaction by pairs, leading to isolation of reactive units. The loss in unsaturation due to

cyclization has been calculated statistically by the method of Flory and Wall, and has been shown to be consistent with the total amount of additive chlorine in the fully chlorinated product.

Cyclization takes place in the early stages of the chlorination simultaneously with the initial substitution. The theoretical limit of cyclization calculated statistically is 86.5 per cent of all isoprene units cyclized for natural rubber and 72 per cent for polyisoprene containing 10 per cent vinyl side chains.

Iodine chloride titration gives fair results for samples of low chlorine content, but is not applicable to polymers containing much more than 35 per cent of chlorine. Knowing the degree of cyclization, the unsaturation can, however, be calculated for any polymer from the extent of additive reaction.

Substitutive chlorination is catalyzed by oxygen and peroxide, additive chlorination by ultraviolet light. Cyclization is partially prevented by the increase in additive reaction. Under the combined effect of peroxides and ultraviolet radiation, chlorination can be carried to very high degrees.

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VOLUMETRIC OXYGEN-ABSORPTION TEST FOR RUBBER AGING *

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The utility and limitations of oxygen-absorption methods for the study of the aging of rubber have been discussed in a previous publication from this laboratory[1]. It was concluded, on the basis of the evidence available at that time, that the volumetric method is generally more reliable than either the gravimetric or manometric method. Most of the examples cited in the previous publication involved GR-S vulcanizates, and it was therefore desired to extend the evaluation of the method to see if it could be used effectively with natural rubber stocks.

The present study includes: (1) an evaluation of the effect of cure on the oxidizability of Hevea rubber vulcanizates; (2) the effect of an antioxidant (Santoflex-B) and a deactivator (mercaptobenzimidazole); and (3) a comparison of a volumetric oxygen-absorption test with the air oven and oxygen-bomb aging tests.

PROCEDURE

The apparatus and procedure employed for the oxygen-absorption measurements have been described[2].

The samples are suspended in an absorption tube which is placed in a constant-temperature aluminum heating block maintained at 100° C. Lump calcium oxide is present to absorb water and carbon dioxide. The oxygen pressure is maintained at 760 mm. by periodic manual adjustment, and the volume of oxygen absorbed is measured by means of a gas buret attached to the absorption tube. Duplicate tubes are included in each run. The data are calculated to cc. of oxygen (25° C, 760 mm.) absorbed per gram of rubber in the compound.

The Hevea black vulcanizates used for this study were compounded as indicated in Table I. Stock A is the control, with no added antioxidant. Stock B is the same with inhibitor added. Stocks C and D have the same composition as A and B except for the addition of mercaptobenzimidazole. The cures were for 20, 40, and 80 minutes at 280° F, in slabs of nominally 0.040-inch thickness.

The values for the initial physical properties of these stocks are given in Table II. Because an acidic accelerator (Santocure) was used, retardation of the vulcanization process due to the presence of mercaptobenzimidazole was to be expected in view of published statements regarding this effect[3]. The properties of stocks C and D which contained mercaptobenzimidazole are lower than those of the corresponding stocks A and B. Nevertheless, the breaks in

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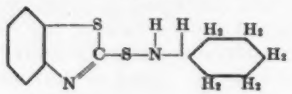
TABLE I

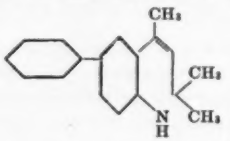
COMPOSITION OF STOCKS

	A	B	C	D
Smoked sheet rubber	100	100	100	100
Paraflux	4	4	4	4
Stearic acid	3	3	3	3
Zinc oxide	3	3	3	3
Santocure[a]	1	1	1	1
Sulfur	3	3	3	3
EPC black	50	50	50	50
Santoflex-B[b]	—	1.5	—	1.5
Mercaptobenzimidazole	—	—	1	1

[a] Reaction product of cyclohexylamine and mercaptobenzothiazole:



[b] Reaction product of acetone and *p*-aminobiphenyl, mainly 2,2,4-trimethyl-6-phenyl-1,2-dihydroquinoline:



the curves of cure *vs.* modulus indicate that the optimum cure is in the vicinity of 50 minutes at 280° F for all four stocks.

Dumbbell tensile specimens were cut from the vulcanized sheets and aged by the three methods: (1) oxygen absorption at 100° C and 750 mm.; (2) circulating air oven at 100° C; and (3) oxygen bomb at 70° C and 300 pounds per square inch. Samples were removed after appropriate time intervals in

TABLE II

INITIAL PHYSICAL PROPERTIES

Stock	Cure	Hardness (shore A durometer)	Stress 200%	Stress 300%	Tensile strength (lb./sq. inch)	Ultimate elongation (%)
A	20	56	840	1480	4160	580
	40	64	1100	1930	3930	500
	80	64.5	1100	1870	3610	470
B	20	56	650	1320	4030	610
	40	63	1050	1840	4080	530
	80	63	1010	1820	3770	490
C	20	53	490	1010	3980	660
	40	58	790	1430	4160	600
	80	59.5	900	1540	3990	570
D	20	53	550	990	4200	680
	40	58	710	1320	4200	620
	80	59	810	1420	3910	580

A. Hevea black uninhibited
B. Hevea black inhibited
C. Stock A + 1 part per hundred MBI
D. Stock B + 1 part per hundred MBI

each case and tested to determine changes in tensile strength, stress at 200 and 300 per cent elongation, elongation at break, and Shore A hardness.

The effect of cure and of compounding variations on the oxygen absorption of these stocks is discussed in the following sections, after which the three aging methods are compared from the point of view of the effect of these same variables.

EFFECT OF CURE

The state of cure has an important effect on the aging of rubber vulcanizates as measured by change in physical properties. If oxygen absorption data are to be used to predict the aging behavior of rubber stocks, it is important to establish the effect of cure on the results obtained with this test. It has been established previously in this laboratory[4] that the effect of curing time on the

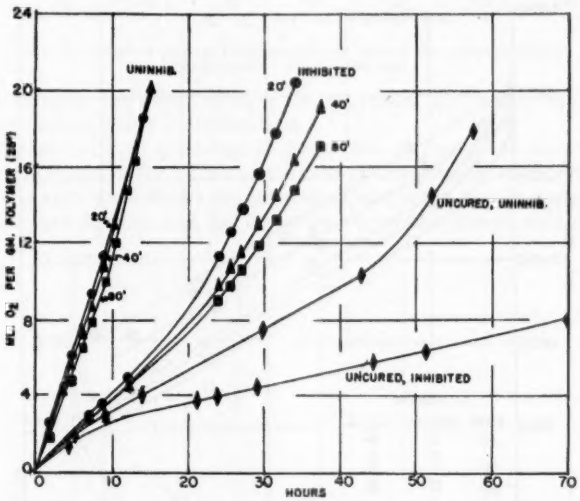


FIG. 1.—Effect of cure on oxygen absorption of Hevea black stocks. 100° C, 760 mm.

rate of oxygen absorption is relatively small in the case of a GR-S vulcanizate. Kohman[5] demonstrated a greater effect in the case of a simple rubber-sulfur vulcanizate.

The present study was confined to Hevea black stocks. Three cures were employed with both the uninhibited (A) and inhibited (B) stocks. Because the optimum cure was approximately 40 minutes at 280° F, the times selected were 20, 40, and 80 minutes, so as to include both an undercure and an overcure.

Effect of cure on oxidation rate.—Figure 1 shows the oxygen absorption curves obtained at 100° C for the three cures of each of two stocks. In each case an uncured strip of the compounded stock was included for comparison. The uncured stocks are considerably more resistant to oxidation than the vulcanizates. A possible explanation which accounts for at least a part of this difference is the presence of natural antioxidants in the natural rubber, which are apparently deactivated during the vulcanization process. The oxygen absorbed in 10 hours was only 3 cc. per gram for the uncured uninhibited

stock, but after vulcanization the absorption was 12 cc. in 10 hours. The proportional increase is much less in the case of the stocks to which the more stable inhibitor, Santoflex-B, was added.

The effect of cure beyond the first 20 minutes at 280° F is relatively small. Nevertheless, in each case additional changes, which take place as the curing time is extended, serve to reduce the rate of oxygen absorption. This is in partial agreement with the results previously obtained[4] with GR-S, in which case the overcures were also observed to absorb less oxygen than the optimum cures. These results are contrary to those observed by Kohman[5] and by Kemp, Ingmanson, and Mueller[6], who found that increase in vulcanization time caused increased oxidizability. These investigators, however, studied gum stocks, whereas the present data were obtained with black stocks. In the case of the uninhibited stock, the longer the cure, the steeper is the slope after an absorp-

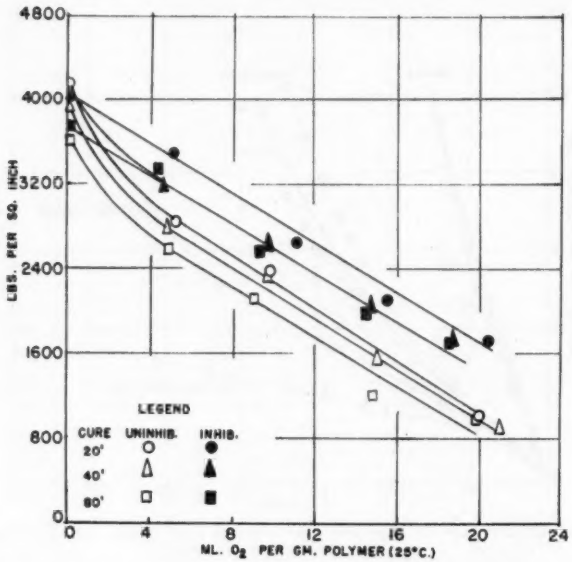


FIG. 2.—Effect of cure on tensile strengths of Hevea black stocks vs. oxygen absorption. 100° C, 760 mm.

tion of 10 cc. of oxygen per gram of rubber has been reached. Consequently, a reversing of the order of the curves is to be expected when an absorption somewhat greater than 20 cc. per gram of rubber has been attained. Nevertheless, at this point, the stock has become so deteriorated that it is no longer of practical value. This reversing of the order of the curves is not evident in the case of the inhibited stocks.

From a practical point of view, it should be recognized that the time of cure, within the ranges studied, has a relatively small effect on the rate of oxygen absorption for a given stock of both natural rubber and GR-S. The effect is actually much less than the effect of cure on the initial values of such physical properties as tensile strength. This is one of the outstanding points in which the oxygen absorption method is superior to aging tests based on changes in

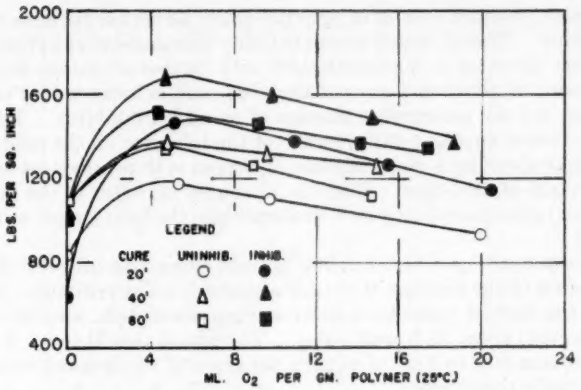


FIG. 3.—Effect of cure on 200% modulus *vs.* oxygen absorption of Hevea black stocks. 100° C, 760 mm.

properties, because the effect of cure on the initial properties frequently obscures other factors under consideration.

Effect of Cure on Rate of Change in Properties.—Changes in tensile strength are plotted in Figure 2 for various amounts of oxygen absorbed. In each set of curves, the undercure shows the highest value for the tensile strength at any given oxygen absorption, and the overcure shows the lowest value; but after

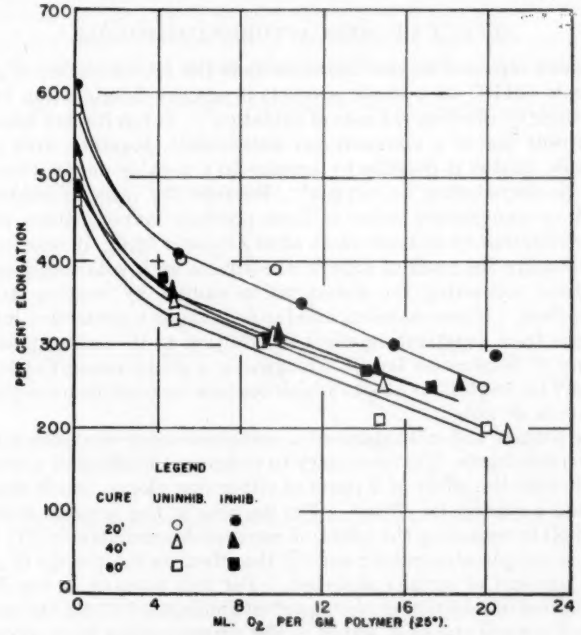


FIG. 4.—Effect of cure on ultimate elongation of Hevea black stocks *vs.* oxygen absorption. 100° C, 760 mm.

the absorption of about 4 cc. of oxygen per gram, all six curves have essentially the same slope. Thus it would seem that after this amount of oxygen has been absorbed, the decrease in tensile strength with further oxidation depends only on the amount of additional oxygen absorbed, and is independent of both the time of cure and the presence or absence of an added inhibitor. The effect of the initial state of cure and the presence of the inhibitor on the relative breakdown brought about by a given amount of oxygen is thus prevalent only during the early stages of oxidation. There is, of course, an effect of the inhibitor on the rate of oxygen absorption which continues into the later stages, as was shown in Figure 1.

Changes in modulus or stress at 200 per cent elongation are plotted in Figure 3 as a function of the amount of oxygen absorbed. The optimum (40-minute) cure gives the highest value for a given oxygen absorption, and the undercure (20-minute cure) gives the lowest value. The curves pass through a maximum at an absorption of 4 to 5 cc. of oxygen per gram of rubber, and then decrease at an essentially linear rate.

The changes in ultimate elongation with amount of oxygen absorbed, as shown in Figure 4, confirm the observation made above with respect to tensile strength, namely, that the rate of change is not affected appreciably by either time of cure or the presence of the added inhibitor. Apparently the inhibitor merely slows down the total oxidation process, and does not appreciably affect the ratio of chain scission and cross linking. Differences in the state of cure are reflected in the initial values but not in the change produced by a given amount of oxygen after the absorption of the first 4 or 5 cc. of oxygen per gram of rubber.

EFFECT OF MERCAPTOBENZIMIDAZOLE

It has been reported in the literature that the incorporation of mercaptobenzimidazole (MBI) in a stock protects it against deterioration by oxygen, while only slightly affecting the rate of oxidation[7]. It has further been reported that concurrent use of a conventional antioxidant, together with mercaptobenzimidazole, makes it possible to increase to a notable degree the resistance of a stock to degradation by oxygen[8]. Because the rates of oxidation were determined by manometric means in these previous investigations, and deterioration was determined in most cases after air-oven aging, it was thought desirable to measure the rates of oxygen absorption by a volumetric method, at the same time measuring the deterioration caused by varying amounts of oxygen absorbed. If mercaptobenzimidazole imparts a protective influence to rubber stocks by a deactivating effect in addition to its antioxidant activity, then the rate of decrease in tensile strength for a given amount of oxygen absorbed should be less for the stocks which contain mercaptobenzimidazole than for those which do not.

To demonstrate the advantage of a combination of the antioxidant with mercaptobenzimidazole, it is customary to compare the effect of a mixture of 1 part of each with the effect of 2 parts of either one alone. Such studies have demonstrated a synergistic effect[9]. The purpose in the present study was to check two points regarding the effect of mercaptobenzimidazole: (1) the effect on the rate of oxygen absorption; and (2) the effect on the change in properties for a given amount of oxygen absorbed. For this purpose it was decided to observe the effect of addition of mercaptobenzimidazole to both the uninhibited and inhibited control stocks A and B. The corresponding mercaptobenzimidazole stocks are designated C and D, as noted in Table I.

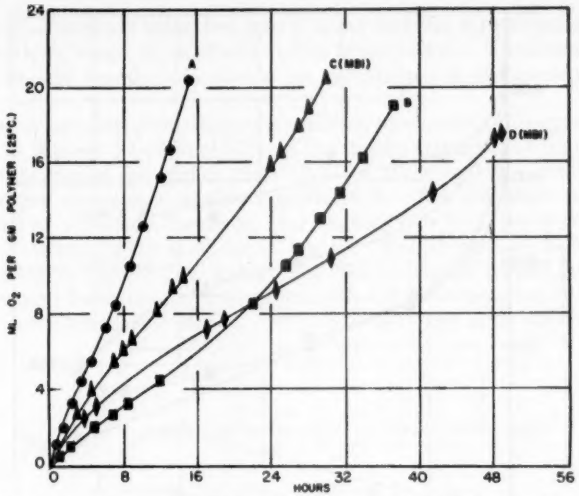


FIG. 5.—Oxygen absorption of Hevea black stocks. 100° C, 760 mm. Effect of incorporation of mercaptobenzimidazole in 40-minute cures.

The oxygen absorption curves obtained with the 40-minute cures are shown in Figure 5. It is apparent that mercaptobenzimidazole causes a very significant decrease in the rate of oxygen absorption when compared to the uninhibited control stock. When added to the inhibited stock, the mercaptobenzimidazole actually caused a slightly more rapid initial rate of oxygen absorption,

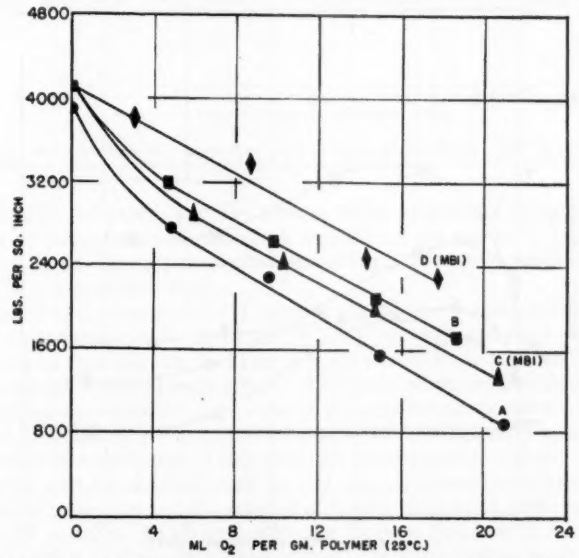


FIG. 6.—Tensile strengths of Hevea black stocks *vs.* oxygen absorption. 100° C, 760 mm. Effect of incorporation of mercaptobenzimidazole in optimum (40-minute) cures.

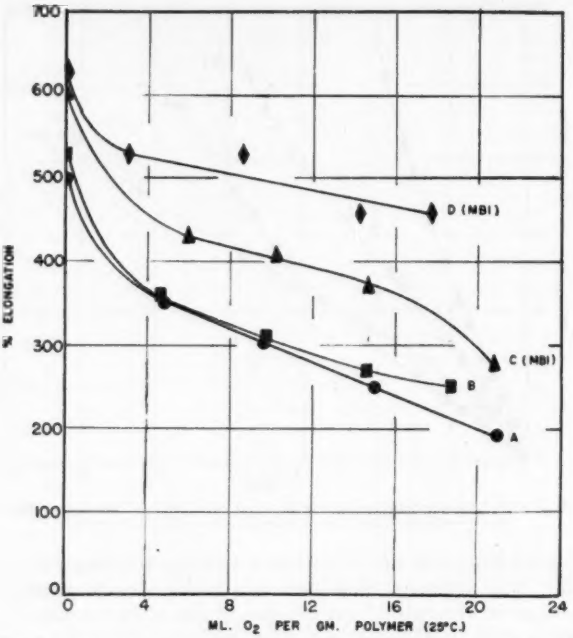


FIG. 7.—Ultimate elongation *vs.* oxygen absorption of Hevea black stocks. 100° C, 760 mm. Effect of incorporation of mercaptobenzimidazole in optimum (40-minute) cures.

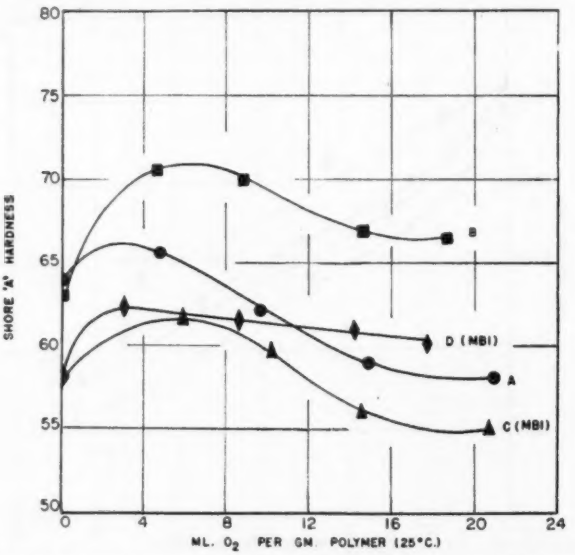


FIG. 8.—Hardness *vs.* oxygen absorption of Hevea black stocks. 100° C, 760 mm. Effect of incorporation of mercaptobenzimidazole in optimum (40-minute) cures.

but in the constant-rate stage the rate is lower and the time required to enter the autocatalytic stage of rapid absorption is increased. Thus mercaptobenzimidazole clearly functions in part as an antioxidant in the usually accepted sense.

Changes in physical properties as a function of amount of oxygen absorbed are shown in Figures 6 to 9, inclusive. The tensile strengths of the mercaptobenzimidazole stocks are higher than those of the respective controls at all levels of oxygen absorption, as shown in Figure 6. The difference arises in the initial period of oxidation, however, and beyond 4 to 5 cc. per gram the rate of change is essentially the same for all stocks. The elongation, hardness, and modulus curves in Figures 7, 8, and 9 show higher elongations and lower values for hardness and for stress required to produce a given elongation in the case of the mercaptobenzimidazole stocks. Approximately the same differences were

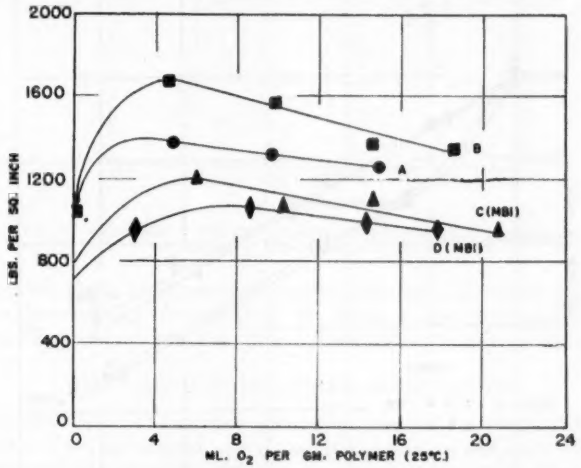


FIG. 9.—200% Modulus *vs.* oxygen absorption of Hevea black stocks. 100° C, 760 mm. Effect of incorporation of mercaptobenzimidazole in optimum (40-minute) cures.

present initially, however, and the change with amount of oxygen absorbed appears to be comparable for stocks A and C and for stocks B and D. The combination in D changes somewhat less than the control stock B, but the difference in rate is rather small.

It will be shown subsequently (Figure 12) in the comparison with oven aging that the mercaptobenzimidazole stocks retain their tensile strength better than the controls and that the combination is more effective than either the antioxidant or mercaptobenzimidazole alone. This is in agreement with the work of Le Bras and his co-workers[10]. In view of the regular relationship of change in properties to amount of oxygen absorbed, as shown in Figures 6 to 9, it appears that the observed superiority of the mercaptobenzimidazole stocks is accounted for at least in part by the decreased rate of oxygen absorption when mercaptobenzimidazole is present. It is only in the early stages of oxidation that an unusual effect seems to be present, and this raises a question as to whether or not the initial state of the vulcanizate may be different when mercaptobenzimidazole is present.

It is apparent from Table II that the mercaptobenzimidazole stocks do not attain a modulus comparable to that of the controls at the optimum (40-minute) cure, even when the cure is extended to 80 minutes, and the shape of the cure curve indicates that additional overcure would not appreciably increase these values. Thus it is not feasible to attain a state of cure with the mercaptobenzimidazole stocks, such that the properties are comparable to the controls at the optimum. However, the 20-minute cures (undercures) for stocks A and B have initial properties which are of approximately the same magnitude as those attained in 80-minute cures (overcures) with stocks C and D. It is, therefore, of interest to compare the changes in physical properties with amount of oxygen absorbed by these stocks when cured to comparable physical properties. It is apparent from Figure 10 that the change in tensile strength with the

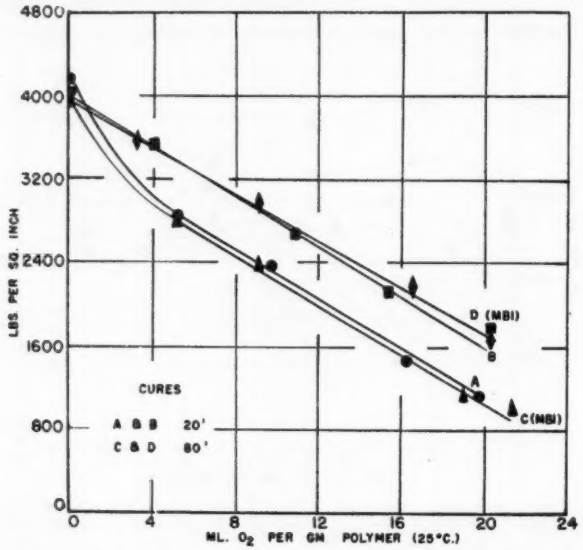


FIG. 10.—Tensile strengths of Hevea black stocks *vs.* oxygen absorption. 100° C, 760 mm. Effect of incorporation of mercaptobenzimidazole in stocks cured to similar original physical properties.

amount of oxygen absorbed is essentially the same with and without mercaptobenzimidazole, regardless of the presence (stocks B and D) or absence (stocks A and C) of a conventional type antioxidant, when the stocks are cured to comparable initial properties. It seems unlikely that this agreement would be the result of chance.

These data indicate that the observed protection imparted by mercaptobenzimidzaole is due to a combination of two factors: (1) the antioxidant activity which reduces the amount of oxygen absorbed, and (2) the effect on the nature of the cure attained. The latter effect should not be confused with effect of time of cure, which is small; it is rather an effect on the nature of the vulcanizate obtained when mercaptobenzimidazole is present. The observed rate of deterioration is, in general, proportional to the rate of oxygen absorption, except in the early stages where the initial state of vulcanization may account for the apparent superiority of the mercaptobenzimidazole stocks.

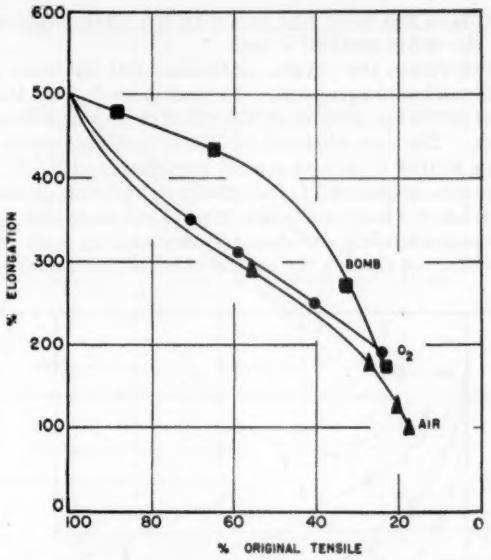


FIG. 11.—Variation of ultimate elongation with loss in tensile strength. Comparison of three aging methods.

Thus, it appears that the effect of mercaptobenzimidazole which has been described as a deactivating effect may be the result of the effect of this material on the vulcanization process rather than a direct effect on the oxidation process.

COMPARISON WITH OTHER AGING TESTS

The potential use of the oxygen absorption method for evaluation of aging characteristics of rubber compounds makes it essential to establish the relationship to other methods of accelerated aging. This is important both to establish

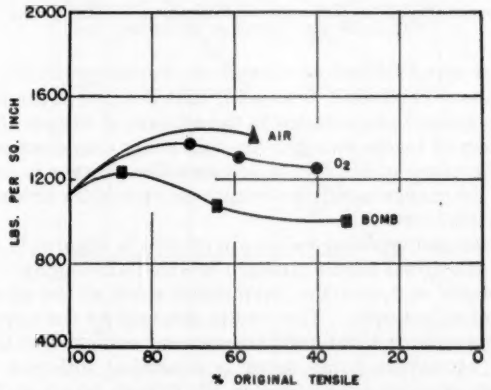


FIG. 12.—Variation of 200% modulus with loss of tensile strength. Comparison of three aging methods.

the relative merits of the tests, and to aid in the interpretation of the results obtained when the newer method is used.

In the present study, the oxygen absorption test has been compared with air oven and oxygen bomb aging test. The compounds were the same as those employed in the preceding studies on the effect of mercaptobenzimidazole and the effect of cure. The data obtained by the oxygen absorption test at 100° C, by air oven aging at 100° C, and by oxygen bomb aging at 70° C and 300 pounds per square inche are compared: (1) from the point of view of the relative effect of the three methods of aging on changes in physical properties; (2) with respect to the effect of compounding variations as revealed by each test; and (3) on the basis of the effect of cure on the results obtained with each test.

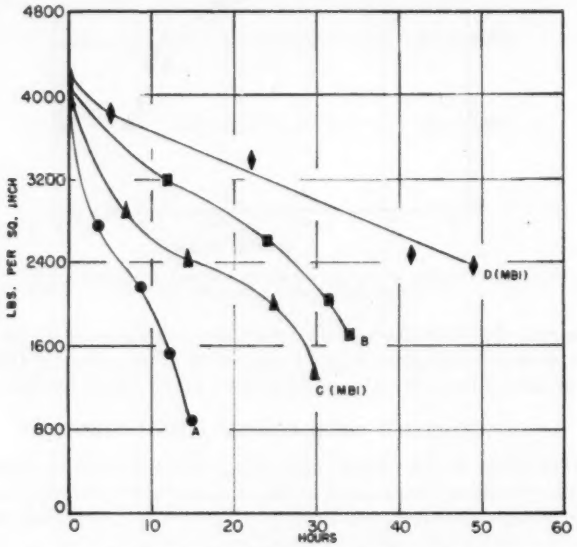


FIG. 13—Tensile strengths of Hevea black stocks *vs.* aging in oxygen. 100° C, 760 mm. Optimum (40-minute) cures.

Effect of three aging methods on changes in physical properties.—It has been demonstrated above (Figures 2, 6, and 10) that changes in the tensile strength of a stock are in general proportional to the amount of oxygen absorbed. Furthermore, changes in tensile strength are commonly employed as a criterion of aging. It is, therefore, of interest to compare the changes in other properties as a function of the change in tensile strength for each of the three aging methods under investigation.

The elongation and modulus values are plotted in Figures 11 and 12 against the percentage of original tensile strength retained after aging. All the stocks gave similar results, and only the uninhibited stock at the 40-minute cure is shown by way of an example. The results obtained by the oxygen absorption and air oven methods (both at 100° C) are very similar, but the relationship brought about by oxygen-bomb aging is somewhat different. For a given change in tensile strength after aging in the oxygen bomb at 70° C and 300 pounds per square inch, the elongation is higher and the modulus lower than the

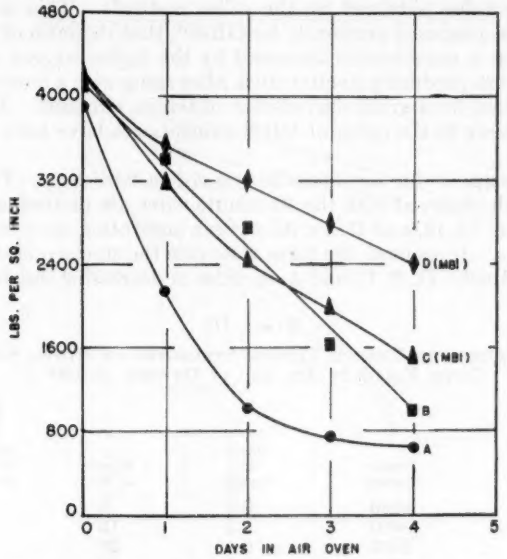


FIG. 14.—Tensile strengths of Hevea black stocks *vs.* aging in air oven. 100° C. Optimum (40-minute) cures.

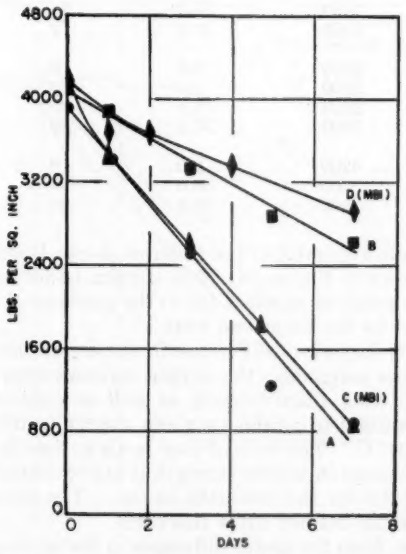


FIG. 15.—Tensile strengths of Hevea black stocks *vs.* aging in oxygen bomb. 300 pounds per square inch, 70° C. Optimum (40-minute) cures.

corresponding value obtained by the other methods. This would seem to indicate, as was proposed previously for GR-S[11], that the ratio of chain scission to cross-linking is considerably increased by the higher oxygen concentration of the bomb, thus producing a softer stock after aging with a lower modulus and higher elongation for a given degradation of tensile strength. These observations with respect to the aging of GR-S vulcanizates have been confirmed by Scott[12].

Effect of compounding variations as reflected in three tests.—The changes in tensile strength observed with the 40-minute cures are plotted against time of aging in Figures 13, 14, and 15, for the oxygen absorption, air oven, and oxygen bomb methods. In general, the three tests rate the stocks qualitatively in the same order, namely, D, B, C, and A, in order of decreasing resistance to aging.

TABLE III

TIMES REQUIRED TO REDUCE TENSILE STRENGTHS OF HEVEA STOCKS TO A GIVEN VALUE IN AIR AND IN OXYGEN AT 100° C

Stock	Tensile strength	Hours in oxygen	Hours in air	Ratio hours in air to hours in oxygen at 100° C
A	3930	0.0	0	—
	3000	2.2	12	5.4
	2400	6.4	20	3.1
	1800	10.8	30	2.7
	1200	13.6	43	3.1
B	4080	0.0	0	—
	3000	16.1	34	2.1
	2400	27.3	54	2.0
	1800	33.3	72	2.2
C	4160	0.0	0	—
	3000	5.6	29	5.2
	2400	15.3	49	3.2
	1800	27.2	80	3.0
D	4200	0.0	0	—
	3000	30.0	58	1.9
	2400	48.2	96	2.0

The only exception is a reversal of the order of stocks B and C after 3 days in the air oven, as shown in Figure 14. The oxygen bomb test (Figure 15) does not demonstrate as much of an effect due to the presence of mercaptobenzimidazole as is indicated by the other two tests.

Because the only important difference in the conditions of the oxygen absorption and air oven methods is the oxygen concentration, it is of interest to compare these two tests quantitatively as well as qualitatively. Table III shows the times required to produce a given change in tensile strength in air and in oxygen at 100° C. The ratio of time in air to time in oxygen required to produce the same change in tensile strength is approximately 3.0 for the uninhibited stocks and 2.0 for the inhibited stocks. The presence or absence of mercaptobenzimidazole did not affect this ratio.

It would appear, from the above difference in the air-oxygen ratio, that the 0.040-inch sample thickness employed is sufficiently great to bring about some limitation of the oxidation reaction by rate of diffusion in the case of the unin-

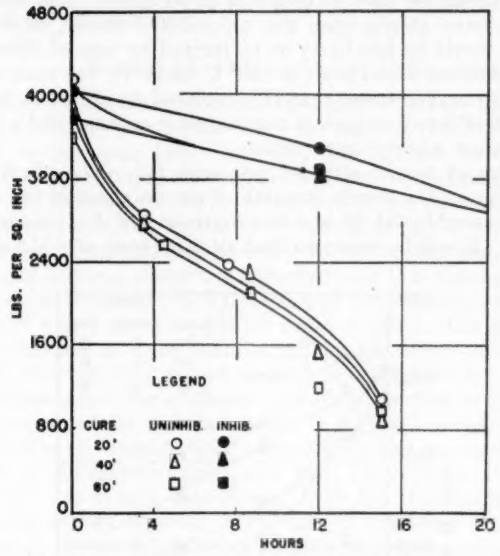


FIG. 16.—Effect of cure on tensile strengths of Hevea black stocks *vs.* aging in oxygen. 100° C, 760 mm.

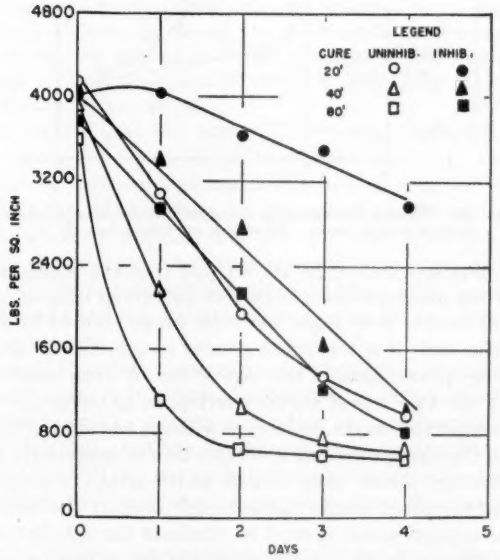


FIG. 17.—Effect of cure on tensile strengths of Hevea black stocks *vs.* aging in air oven. 100° C.

hibited stocks in air at 100° C (but not in oxygen). The inhibited stocks oxidized much more slowly than the uninhibited stocks, and consequently their oxidation would be less likely to be limited by rate of diffusion. In the case of the uninhibited stocks in air at 100° C, however, the more rapid reaction probably uses up oxygen faster than it is replaced by diffusion, with the result that the concentration of oxygen in the sample is reduced and a longer time is required to produce a given deterioration.

Effect of cure on results obtained with each test.—The effect of the three methods of aging on the tensile strength of the uninhibited (A) and inhibited (B) compounds cured for 20, 40, and 80 minutes at 280° F is presented in Figures 16, 17, and 18. It will be observed that all three tests give the same order for

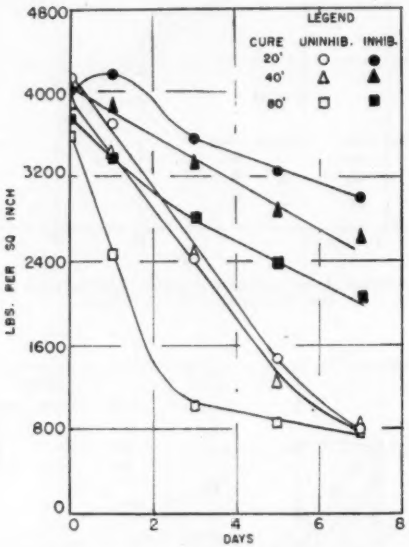


FIG. 18.—Effect of cure on tensile strengths of Hevea black stocks as aging in oxygen bomb. 300 pounds per square inch, 70° C.

the cures in each case, namely, 20, 40, 80, and that the tensile strength of the stock cured for the shorter time is higher at any given time of aging.

The effect of cure is very slight over the range studied in the case of the oxygen absorption test; it is somewhat greater in the case of the oxygen bomb test; and it is very pronounced in the case of the air oven method. In Figure 17, for example, the two sets of curves overlap, so the overcure with inhibitor appears to be comparable to the undercure without added inhibitor. Thus, the effect of cure on the aging behavior is comparable in magnitude to the effect of the antioxidant when the air oven is used as the criterion of aging resistance. It is evident that the effect of cure may seriously obscure the results when either the air oven or oxygen bomb is used to evaluate the relative merits of antioxidants or the effect of other compounding variations upon aging behavior.

The fact that cure has relatively little effect on either the rate of oxidation or the rate of tensile deterioration when the oxygen absorption method is used

is thus an outstanding advantage in all aging studies, other than those directly concerned with the effect of cure.

SUMMARY AND CONCLUSIONS

A volumetric oxygen-absorption test for aging of rubber has been investigated from the point of view of the effect of cure and the effect of mercaptobenzimidazole on the aging behavior. The test has also been evaluated by comparison with conventional air oven and oxygen bomb aging.

A compounded but uncured Hevea black stock is more resistant to oxidation than the vulcanized material, but after a reasonable cure is obtained, further heating produces only a small change in the rate of oxygen absorption.

The change in physical properties corresponding to a given amount of oxygen absorbed varies somewhat with time of cure in the initial stages, but after the absorption of 4 or 5 cc. of oxygen per gram of rubber, the changes in most physical properties are a direct function of the amount of oxygen absorbed. Neither time of cure nor the presence or absence of inhibitor has any significant effect on the subsequent rate of change in such properties as tensile strength and ultimate elongation for a given amount of oxygen absorbed.

Oven aging data on identical time cures confirm the reported superiority of a combination of mercaptobenzimidazole with a conventional type of antioxidant. Oxygen absorption data reveal, however, that mercaptobenzimidazole causes a significant decrease in the rate of oxidation of a Hevea black stock, and thus it clearly functions at least in part as an antioxidant in the usually accepted sense.

The deterioration of properties is, in general, proportional to the oxygen absorbed, except in the early stages of oxidation where the mercaptobenzimidazole stocks change somewhat less than the controls for a given amount of oxygen absorbed. When the cures are selected to give comparable initial properties, however, the change in tensile strength of the mercaptobenzimidazole stocks with amount of oxygen absorbed is essentially the same as for the controls, even in the initial stages.

These data suggest that the observed protection imparted by mercaptobenzimidazole results from a combination of two factors: (1) the normal antioxidant activity of mercaptobenzimidazole, which reduces the amount of oxygen absorbed; and (2) an effect on the nature of the cure attained when mercaptobenzimidazole is present, such that the absorption of a given amount of oxygen in the early stages is not accompanied by as great a change in properties. Thus, it appears that the deactivating effect may be the result of the effect of this material on the vulcanization process rather than a direct effect on the oxidation process.

A comparison of the effect of oxygen absorption, air oven, and oxygen bomb aging methods on changes in physical properties of Hevea black stocks shows that the results obtained by oxygen absorption and air oven methods (both at 100° C) are similar, but that the higher oxygen concentration of the oxygen bomb test (70° C and 300 pounds per square inch) apparently results in a higher proportion of chain scission when compared to cross-linking of the polymer chains.

The effect of compounding variations as reflected in the three tests is such that the four stocks were rated qualitatively in the same order, in most cases. There was a reversal of the order of two of the stocks after 3 days in the air

oven, however, and the oxygen bomb test does not demonstrate as much of an effect due to the presence of mercaptobenzimidazole as do the other two tests.

The ratio of the time in air to the time in oxygen at 100° C required to produce a given change in tensile strength was approximately 2.0 for the inhibited stocks and 3.0 for the uninhibited stocks, and the presence or absence of mercaptobenzimidazole did not affect the ratio. The higher ratio observed for the uninhibited stocks probably is the result of partial limitation of the oxidation reaction by rate of diffusion in the case of the air oven method.

The effect of cure is very slight over the range studied in the case of the oxygen absorption test; it is somewhat greater in the case of the oxygen bomb test; and it is very pronounced in the case of the air oven method. This is one of the outstanding advantages of the oxygen absorption method for aging studies, since the effect of cure frequently obscures the effect of other factors under investigation when the other aging methods are employed.

No one aging test can be expected to give all the answers required, for example, ozone resistance is a very important factor which is not measured by oxygen absorption. Furthermore, it is generally desirable to evaluate a product under service conditions whenever possible, in addition to the use of accelerated aging tests. Nevertheless, accelerated tests are of value, and the volumetric oxygen absorption test appears to have a greater potential usefulness as a general method for evaluating aging resistance of rubber stocks than the tests now commonly employed for this purpose.

ACKNOWLEDGMENT

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RUBBER OXIDATION AND AGING STUDIES

SAFE LIMITS OF SAMPLE THICKNESS *

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Whenever an accelerated aging test for rubber is employed, it is important to know whether the observed rate of deterioration is determined by the susceptibility of the rubber compound to oxidation or whether the rate is limited by the rate at which oxygen diffuses into the sample under the conditions of the particular test. In kinetic studies involving the rate of oxygen absorption by natural and synthetic rubbers, it is essential to know whether the observed rate is a true measure of the chemical reaction or whether the rate is limited by the physical process of diffusion.

The object of the work reported in this paper is to establish the safe limits of sample thickness at various temperatures for typical natural and synthetic rubber compounds so that chemical reaction, rather than diffusion, will be the controlling factor. Only when two samples of different surface area-to-weight ratios have the same oxygen-absorption curve at a given temperature is it certain that the rate of the chemical reaction alone has been measured. When diffusion is rate controlling, an increased surface area-to-weight ratio results in an increase in the measured rate of absorption.

Standard industrial practice in the determination of oxidation or aging of rubber of all types is to employ samples of approximately 0.080 inch (about 2 mm.) in thickness, with the adjustment of the operating conditions of temperature and oxygen pressure to complete the determination in a relatively short time. This procedure and the results obtained are of considerable value in evaluating relative degrees of oxygen deterioration, but in many instances the data are the result of limitation by diffusion; if this is not recognized, some confusion may be introduced in the interpretation of the results.

The effect of surface area on the rate of oxygen absorption of natural rubber has been noted by previous workers[1], and the effect in a GR-S black stock was discussed briefly in a prior publication from this laboratory[2]. This work extends the study to other temperatures and to other elastomers and seeks to establish more precisely the safe limits of sample thickness for rubber oxidation and aging studies.

A typical oxygen absorption curve for either natural or synthetic rubber vulcanizates shows a short initial period of rapid oxidation, followed by a longer period in which the rate of oxidation is slower and fairly constant, and finally by an autocatalytic stage of more rapid absorption. If the sample thickness is such that the rate is not limited by diffusion in this final rapid stage, then it would clearly be free of limitation in the earlier stages as well. The first efforts were, therefore, directed toward establishing the safe limits of sample thickness for the autocatalytic stage.

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Many oxidation and aging studies are primarily concerned with the earlier stages of oxidation, since the properties of a vulcanizate are seriously degraded long before the autocatalytic stage is reached. Consequently the last portion of this paper also sets forth the approximate sample thickness observed to be free of limitation by diffusion in the constant-rate stage of oxidation.

APPARATUS AND PROCEDURE

The oxygen-absorption apparatus employed for this work is of the volumetric type described in previous publications from this laboratory[3]. The

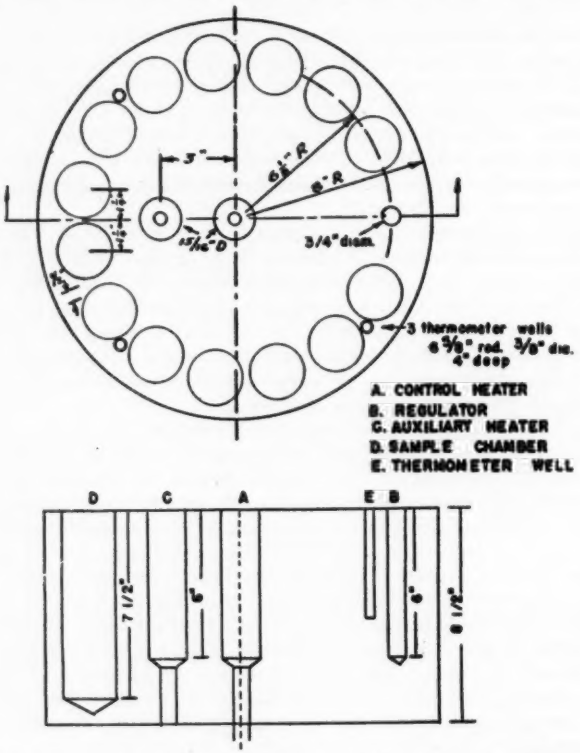

FIG. 1.—Aluminum heating block. Fourteen holes, 2-inch diameter, equally spaced.

most recent modification of the equipment employs an aluminum block (Figure 1) as the source of heat at constant temperature. The auxiliary heater is used only to help bring the block to the desired temperature, and only the control cartridge heater is used during a run. The temperature is controlled within ±0.25° C up to an operating temperature of 150° C. The aluminum block is bored to accommodate fourteen absorption units of the type shown in the detail drawing in Figure 2. Each is attached to a gas buret by a 2-mm. capillary tube. The assembled apparatus is shown in Figure 3. A new-type support for the mercury-filled leveling bulbs, mounted on stainless steel rods, facilitates rapid

and accurate adjustment to obtain the desired pressure in the system. The heating block is covered on all sides with at least 2 inches of insulation.

The procedure has been described fully[2]. However, a few comments relative to techniques developed in the use of the method might be of value to other workers in the field. For example, accurate measurement of the pressure differential is facilitated by directing a beam of light across the surface of the mercury in the leveling bulb so as to cast a shadow on the buret. Tygon tubing is used to join the connecting capillary glass tubes to the sample tube and to the

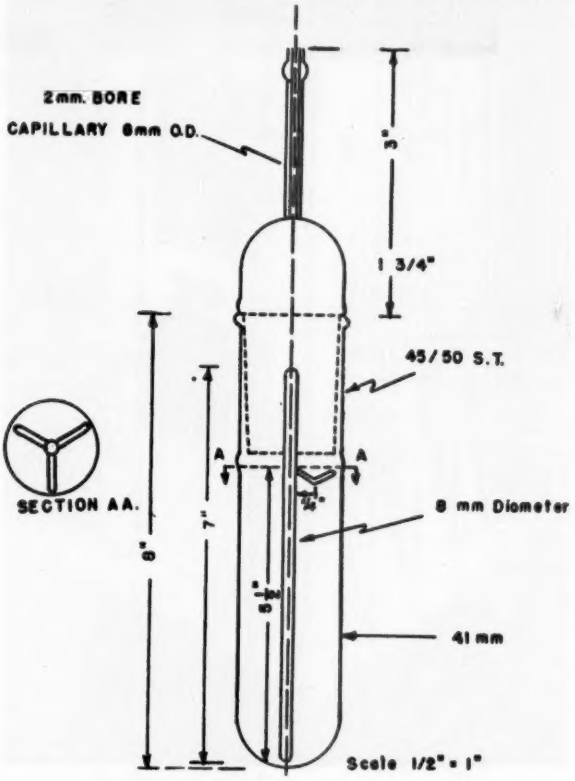

FIG. 2.—Absorption tube.

buret. A little glycerol is employed as a lubricant to aid in slipping the Tygon collar on the glass. Old collars are cut off and new ones used for each run. Any absorption of oxygen by the small amount of exposed Tygon at room temperature is negligible in comparison with the absorption by the rubber at elevated temperature, and in any event the empty control tubes employed would correct for possible error from this source. Cellogrease was originally employed to lubricate and seal stopcocks and ground-glass joints, but this material does oxidize to some extent. Silicone stopcock lubricant has proved more satisfactory for this purpose and is now used exclusively.

As each sample tube is placed in the heating block it is immediately evacuated and held under vacuum until all are in place. Oxygen is then admitted and the system immediately reevacuated. This cycle is repeated three times and the initial volume reading taken immediately after the oxygen has been admitted the last time and the pressure adjusted to 760 mm. of mercury. Subsequent volume changes due to lack of temperature equilibrium at the time of the first reading are corrected by the corresponding changes in the duplicate control tubes.

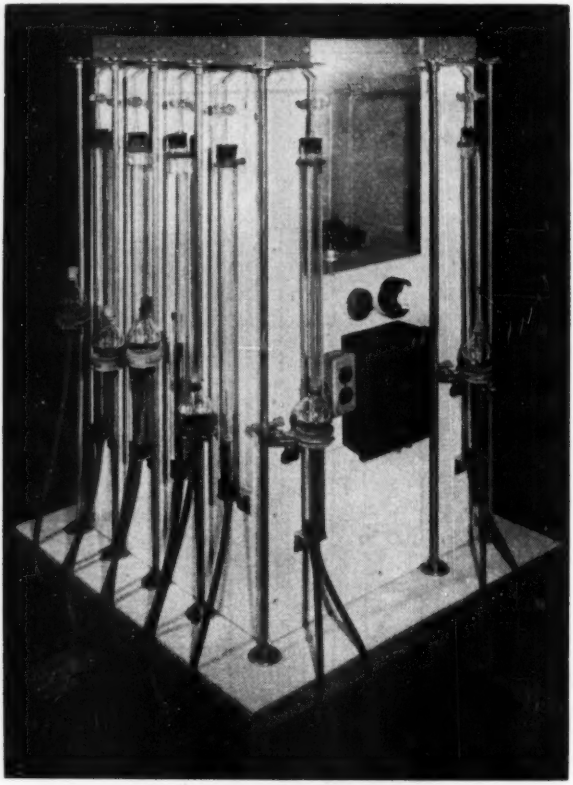

FIG. 3.—Assembled apparatus.

SCOPE OF INVESTIGATION

Natural rubber and three synthetic rubber types, GR-S, Neoprene, and Butaprene-NXM, were included in this study. Both gum and black stocks of each rubber type were prepared and the Hevea black stock was studied both with and without the addition of antioxidant. The composition of the stocks is indicated in Table I.

Each stock was cured in slabs of four different thicknesses, usually within 0.010 to 0.080 inch. The volumetric rate of oxygen absorption was determined for each thickness of each stock at a minimum of three temperatures within

TABLE I

COMPOSITION OF STOCKS

Parts per hundred	GR-S		Smoked sheet			Butaprene-NXM		Neoprene	
Type Stock	Black	Gum	Black	Black	Gum	Black	Gum	Black	Gum
Stock No.	1	2	3	4	5	6	7	8	9
EPC black	50	—	50	50	—	—	—	—	—
SRF black	—	—	—	—	—	60	—	50	—
Santoflex-B[a]	—	—	1.5	—	—	1.5	1.5	1.5	1.5
Stearic acid	1.5	1	3	3	2	—	—	0.5	0.5
Zinc oxide	5	5	3	3	5	5	5	5	5
Santocure[b]	1.2	1.2	1	1	—	—	—	—	—
Thiotax[c]	—	—	—	—	0.75	—	—	—	—
Monex[d]	—	—	—	—	—	0.75	0.75	—	—
Sulfur	2	2	3	3	3	1.75	1.75	—	—
Bardol[e]	5	—	—	—	—	—	—	—	—
Paraflux[f]	—	—	4	4	—	—	—	—	—
Plasticizer-SC[g]	—	—	—	—	—	10	5	—	—
Dibutyl phthalate	—	—	—	—	—	5	—	—	—
Circo light oil	—	—	—	—	—	—	—	2	2
Pip-pip	—	—	—	—	—	—	—	0.25	0.25
Light calcined MgO	—	—	—	—	—	—	—	4	4
Cure time (min.)	50	60	40	40	40	20	20	40	40
Cure temp. (° F)	298	280	280	280	280	280	280	280	280

[a] Reaction product of acetone and p-aminobiphenyl.
[b] Reaction product of cyclohexylamine and mercaptobenzothiazole.
[c] Mercaptobenzothiazole.
[d] Tetramethylthiuram monosulfide.
[e] Obtained from Barrett Div., Allied Chem. and Dye Co.
[f] Obtained from C. P. Hall Co.
[g] Obtained from E. F. Drew & Co.

60° to 150° C. The particular thicknesses and temperatures employed were not the same for all stocks, but were selected arbitrarily for each on the basis of convenience and the anticipated rates of diffusion and oxidation, based on prior experience.

Approximate safe limits of sample thickness were determined by inspection of the graphs of oxygen absorption versus time. More accurate limiting values have been calculated on the basis of a method developed for GR-S stocks[4].

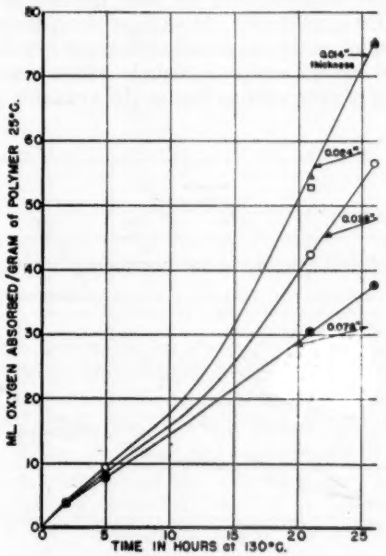

FIG. 4.—GR-S black vulcanizate, 130° C.

LIMITING VALUES FOR AUTOCATALYTIC STAGE

Theory and data for GR-S.—The data for the GR-S black stock was obtained at an earlier date[4], and the oxygen absorption curves obtained at 80°, 90°, 100°, 110°, and 120° C for three different thicknesses have been published[2]. Comparable data obtained at 130° and 150° C are shown in Figures 4 and 5. Figure 6 shows a typical oxygen absorption curve for a GR-S gum stock at 130° C.

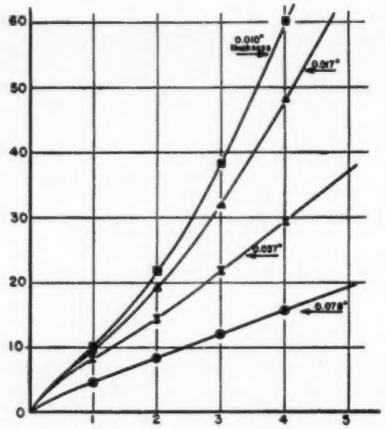

FIG. 5.—GR-S black vulcanizate, 150° C.

Below 100° C the absorption curves for the samples of different thicknesses coincide, and therefore diffusion does not limit the rate of absorption even for samples 0.075 to 0.080 inch thick. At each of the higher temperatures, however, there is a definite maximum sample thickness beyond which the rate of absorption is limited by diffusion. A sample whose absorption is limited by diffusion is absorbing oxygen only as fast as the available surface permits. In

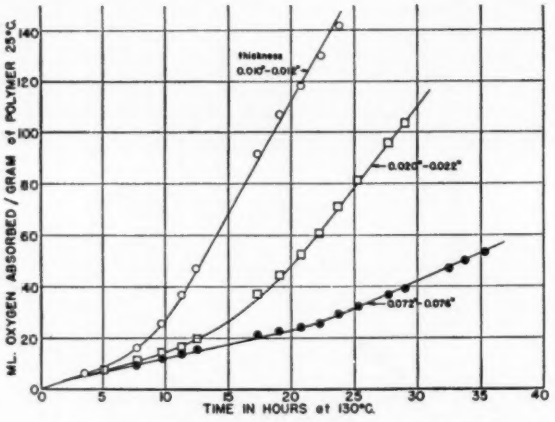

FIG. 6.—Oxygen absorption of GR-S gum stock at 130° C.

such cases, the maximum rate of diffusion expressed as cc./hr./sq. cm. of surface area should be a constant. In Table II the measured maximum rate of absorption per square centimeter of surface area is given for samples of different thicknesses at 110°, 120°, 130°, and 150° C. Since even the thickest samples employed were not limited by diffusion at temperatures up to 100° C, the maximum diffusion rate cannot be calculated from the data obtained at 80°, 90°, and 100° C.

Since the oxygen absorption curves for the two thinnest samples coincide at each temperature except 150° C, and since the rates of diffusion for the thin-

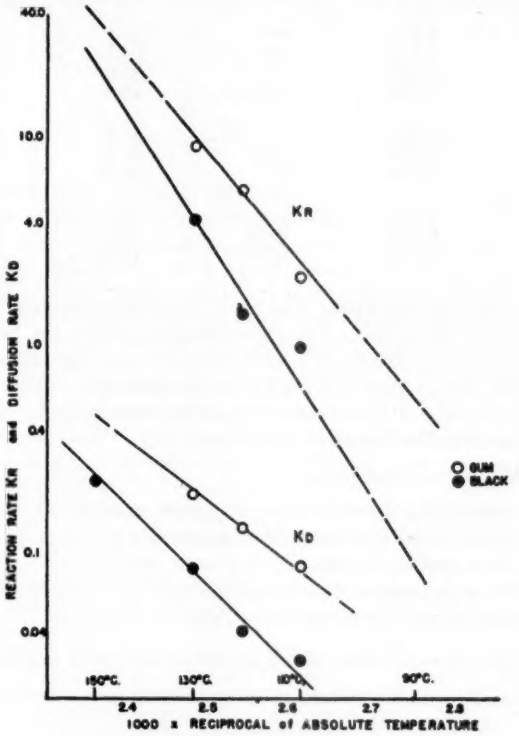

FIG. 7.—Limiting diffusion and reaction rates for GR-S stocks.

nest samples at each temperature, as shown in Table II, are lower than those for the thicker samples, the thin samples are not limited by diffusion. Therefore, the observed rate of absorption for the thinnest samples is in each instance a true measure of the rate of the chemical reaction occurring. The samples which are limited by diffusion, that is, have lower rates of absorption than the thinnest samples, have a constant diffusion rate. The limiting diffusion rates at the various temperatures are as follows: 110° = 0.031, 120° = 0.043, 130° = 0.087, and 150° = 0.23 cc./hr./sq. cm. In Figure 7 the logarithm of the limiting diffusion rate (K_D) and the logarithm of the maximum observed reac-

TABLE II

LIMITING DIFFUSION RATE CALCULATION
(GR-S black vulcanizate)

Temperature (° C)	Thickness (inches)	Obsvd. Max. absorption rate (cc./g./hr.)	Surface area (sq. cm./g. GR-S)	Apparent diffusion rate (cc./hr./sq. cm.)
150	0.010	22.9	127.5	0.180
	0.017	17.5	75.0	0.234
	0.037	7.91	34.5	0.229
	0.078	3.70	16.35	0.228
130	0.014	4.06	91.1	0.045
	0.024	4.06	53.1	0.075
	0.038	2.82	33.6	0.084
	0.076	1.465	16.8	0.087
120	0.026	1.41	49.0	0.029
	0.038	1.41	33.6	0.042
	0.078	0.71	16.35	0.043
110	0.026	0.985	49.0	0.020
	0.038	0.809	33.6	0.024
	0.078	0.506	16.35	0.031

tion rate in cc. per hour per gram (K_R) have been plotted against the reciprocal of the absolute temperature. The corresponding values for the GR-S gum stock as obtained from the oxygen absorption curves obtained at 110°, 120°, and 130° C are also plotted in Figure 7 for comparison. From this plot the limiting thickness for a given temperature may be estimated. The equations may be developed in the following manner:

1. Surface area from thickness:

Let W = weight of polymer in the compound, grams
d = density of the compound = g. per cc.
t = thickness in inches
P = % of polymer in the compound
A = surface area of sample in sq. cm.

Then, neglecting edge effect which can be shown to be negligible:

$$A = \frac{2x\ 100W}{Pdt \times 2.54} = \frac{78.6W}{Pdt}$$

For the compound employed here (GR-S black)

$$d = 1.018\text{g./ml.} \quad P = 60.7\%$$

Since the maximum absorption rates are measured in cc. per gram of polymer, $W = 1.0$

$$\text{Then } A = \frac{78.6 \times 1}{60.7 \times 1.018t} = \frac{1.275}{t}$$

Thus, if the thickness = 0.010 inch, A = 127.5 sq. cm. These data are summarized in Table III for all the stocks employed in this study.

2. Limiting thickness at a given temperature:

From Figure 7 the diffusion constant (limiting diffusion rate) may be obtained for this compound at any temperature in the desired range. In the limiting case the product of the surface area and the rate of diffusion is equal to the rate of reaction.

$$K_D = \frac{K_R}{A} \text{ mathematically}$$

$$\text{since } A = \frac{1.275}{t} \qquad K_D = \frac{K_R t}{1.275} \qquad t = \frac{K_D 1.275}{K_R}$$

Example: at 150° C $\log K_R = 11.36–10 \quad K_R = 23$

$$\log K_D = 9.36–10 \quad K_D = 0.23$$

$$t = \frac{1.275 \times 0.23}{23} = 0.013 \text{ inch}$$

The estimated limiting sample thicknesses at each of the various temperatures calculated in this manner for the GR-S black stock are shown in Figure 18, along with the corresponding values subsequently obtained for the other stocks included in this study. The significance of these thicknesses should be fully understood. They are the maximum thicknesses that permit the diffusion of oxygen into the sample at a rate sufficient to support the chemical reaction at the observed maximum rate for this particular compound, temperature, and 760 mm. of oxygen pressure. It is to be expected that different polymers and different compounding formulations will have different limiting diffusion rates and different maximum reaction rates. Therefore, different limiting thicknesses are to be expected. Furthermore, at reduced pressures both the rates of chemical reaction and diffusion will be different, and the limiting sample thickness may be altered.

Results obtained with other stocks.—Oxygen absorption curves were obtained with various thicknesses of the natural rubber stocks at temperatures ranging from 60° to 110° C. Typical examples are shown in Figures 8, 9, and 10. Maximum observed absorption rates in the autocatalytic stage and the maximum observed diffusion rate, obtained from these data in the same manner as

TABLE III

DATA REQUIRED FOR CALCULATIONS OF LIMITING SAMPLE THICKNESS

Compound	Density (g./cc.)	Polymer (%)	Equation for surface area	Limiting sample thickness
GR-S Black	1.018	60.7	$A = 1.275/t$	$1.275K_D/K_R$
GR-S Gum	0.986	91.4	$A = 0.872/t$	$0.872K_D/K_R$
Hevea Black				
Inhibited	1.11	60.5	$A = 1.17/t$	$1.17K_D/K_R$
Uninhibited	1.08	61.1	$A = 1.19/t$	$1.19K_D/K_R$
Hevea Gum				
Uninhibited	0.969	90.4	$A = 0.899/t$	$0.899K_D/K_R$
Butaprene-NXM				
Black	1.19	54.3	$A = 1.218/t$	$1.218K_D/K_R$
Gum	1.045	87.6	$A = 0.860/t$	$0.860K_D/K_R$
Neoprene (GR-M)				
Black	1.42	61.2	$A = 0.901/t$	$0.901K_D/K_R$
Gum	1.31	88.2	$A = 0.892/t$	$0.892K_D/K_R$

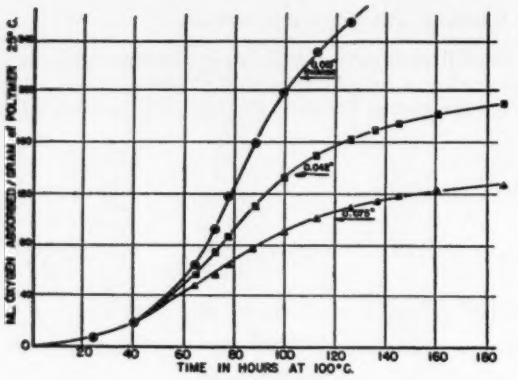

FIG. 8.—Hevea black tread stock, 100° C, antioxidant added.

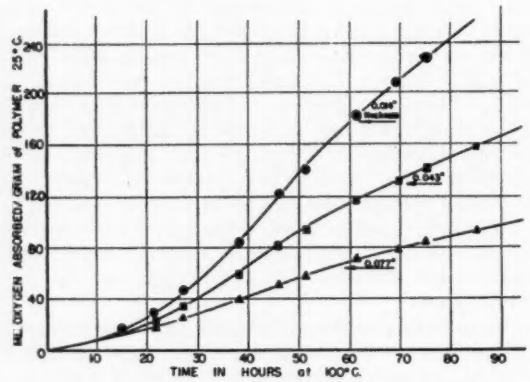

FIG. 9.—Hevea black tread stock, 100° C, no antioxidant.

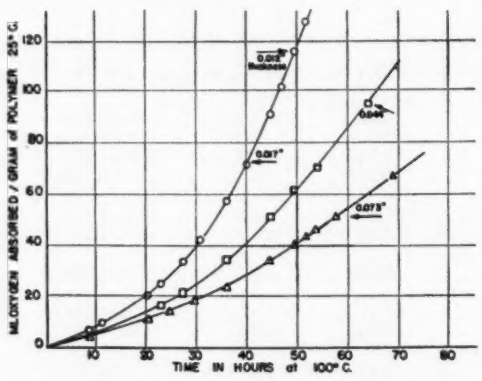

FIG. 10.—Hevea gum vulcanizate, 100° C, no antioxidant.

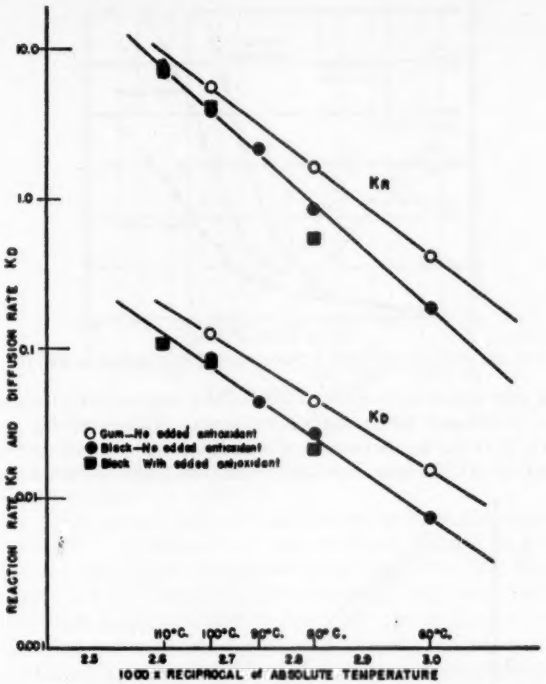

FIG. 11.—Limiting diffusion and reaction rates for Hevea stocks.

explained above for GR-S, have been plotted in Figure 11 as the logarithm of the limiting rates against the reciprocal of the absolute temperature. The limiting values for the Hevea black stock with and without added antioxidant fall along the same straight line when plotted on this basis. This indicates that the antioxidant is used up during the constant-rate stage, and hence there is little or no effect on the ultimate reaction rate obtained in the autocatalytic stage.

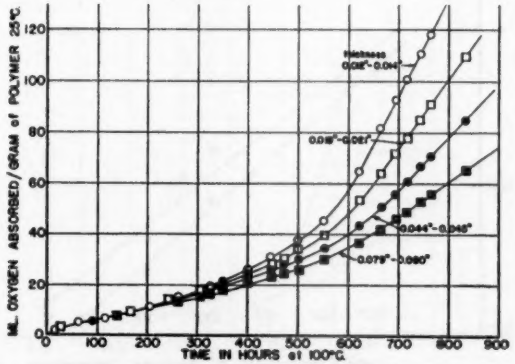

FIG. 12.—Oxygen absorption of Butaprene-NXM black stock at 100° C.

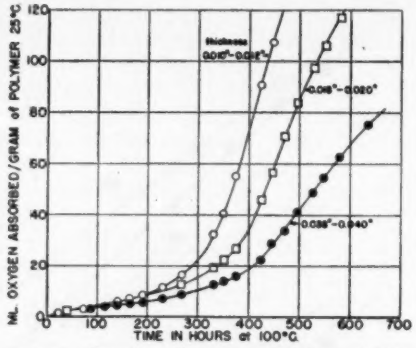

FIG. 13.—Oxygen absorption of Butaprene-NXM gum stock at 100° C.

The upturn in rate apparently corresponds to the point at which the antioxidant concentration is reduced to an ineffective level. Values of K_D and K_R read from Figure 11, both for temperatures within the range studied and for a reasonable extrapolation of the data, have been used with the required data of Table

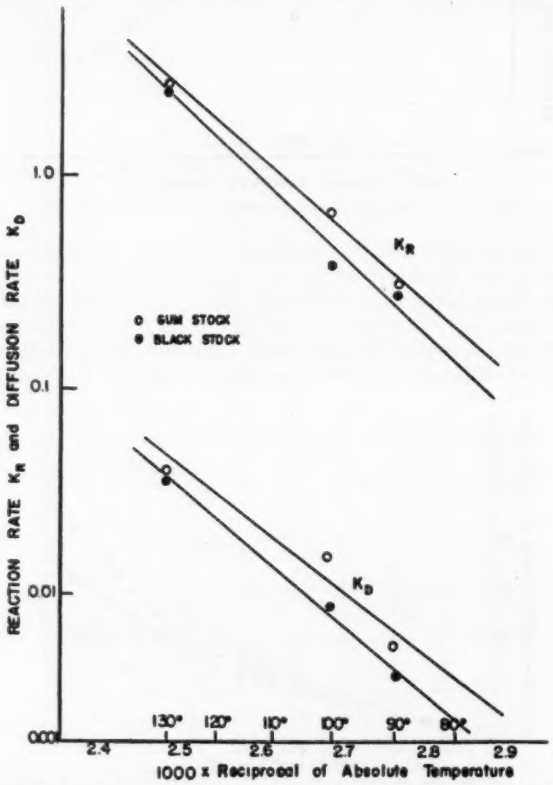

FIG. 14.—Limiting diffusion and reaction rates for Butaprene-NXM stocks.

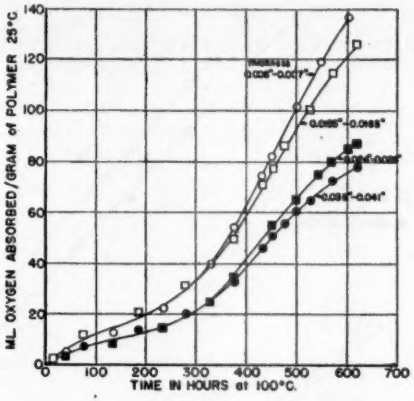

FIG. 15.—Oxygen absorption of Neoprene black stock at 100° C.

III to calculate the limiting sample thickness values shown in Figures 18 and 19 for the Hevea stocks.

Butaprene-NXM stocks were investigated in similar fashion at temperatures from 90° to 130° C. Typical results are shown in Figures 12 and 13. Runs completed first at the higher temperatures revealed that the limiting sample thickness is quite low for those stocks, and consequently some very thin sheets of about 0.005-inch thickness were included in the studies at 90° C. The calculated diffusion rates do not approach a constant value as closely as was observed with GR-S, and the K_D values for the gum stock plotted in Figure 14 do not locate the line so well as might be desired. It is clear that the mathematical relationship developed for GR-S does not apply so well to the Butaprene-NXM stocks. Nevertheless, the calculated values for the limiting sample thickness shown in Figures 18 and 19 appear to be of the right order of magnitude.

The data obtained with various thicknesses of Neoprene black and gum stocks at 90°, 100°, and 110° C are illustrated in Figures 15 and 16 by the re-

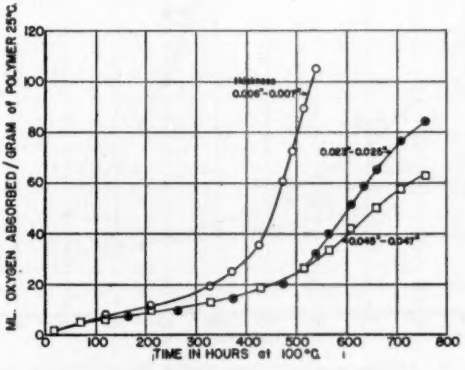

FIG. 16.—Oxygen absorption of Neoprene gum vulcanizate at 100° C.

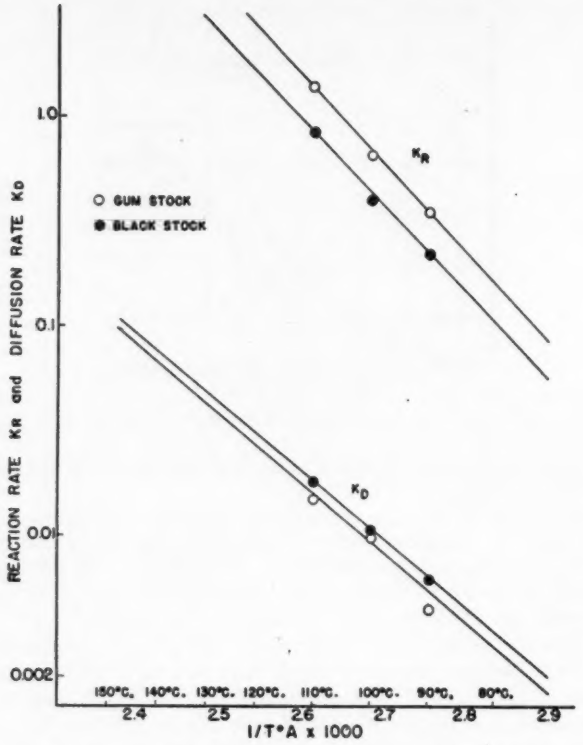

FIG. 17.—Limiting diffusion and reaction rates for Neoprene stocks.

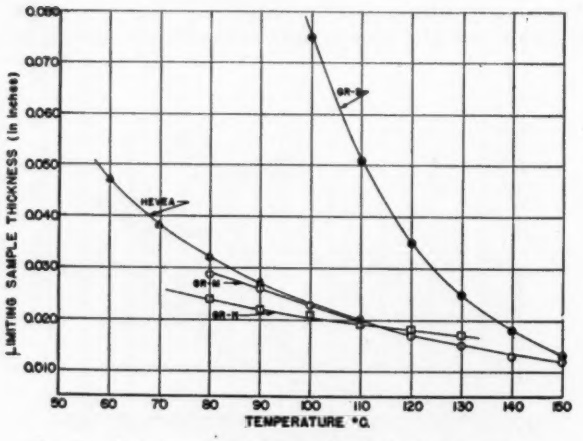

FIG. 18.—Limiting sample thickness of black stocks vs. temperature.

TABLE IV

SAMPLE THICKNESS DEMONSTRATED TO BE FREE OF LIMITATION BY DIFFUSION IN CONSTANT-RATE STAGE

Stock	Temperature (° C)	Thickness shown to be free of limitation (inches)	O_2 absorbed at end of constant-rate stage (cc./g. of polymer)
GR-S black	110	0.075	30
	120	0.040	30
	130	0.040	15
	150	0.020	15
GR-S gum	110	0.075	15
	120	0.075	20
	130	0.020[a]	20
Hevea black	80	0.075	20
Inhibited	100	0.075	20
	110	0.040	20
Uninhibited	60	0.075	20
	80	0.040	20
	90	0.040	25
	100	0.040	20
Hevea gum	60	0.075	25
	80	0.040	20
	100	0.020	20
Butaprene-NXM	90	0.040	15
Black	100	0.040	15
	130	0.015	20
Gum	90	0.040	20
	100	0.020	10
	130	0.010	10
Neoprene (GR-M)	90	0.040[a]	20
Black	100	0.040	20
	110	0.020	15
Gum	90	0.045[a]	15
	100	0.045	15
	110	0.025	12

[a] A somewhat thicker sample might prove satisfactory.

sults obtained at 100° C. The data are somewhat more regular than for the Butaprene-NXM, although some similar difficulties were encountered. The calculated limiting sample thickness values from the graph in Figure 17 and the necessary data of Table III are plotted in Figures 18 and 19.

Prior to the development of the equation used here for calculation of the limiting sample thickness, the broad limits were determined by inspection. If, for example, in a hypothetical case, four different thicknesses were employed—0.010, 0.020, 0.040, and 0.080 inch—and the thinnest two gave virtually identical oxygen absorption curves, it would be obvious that there was no limitation by diffusion for these two thicknesses. If the two thicker samples showed progressively slower maximum rates of absorption as the ratio of surface area to weight decreased, a limitation by diffusion would be indicated. In this instance it would appear that the borderline thickness would be somewhere between 0.020 and 0.040 inch.

The calculations described help to locate the limiting value more accurately within the limits thus established. Nevertheless, the broad limits, which are usually apparent by inspection, serve as a check on the reliability of this method of calculation. Applying this check to all the data summarized in Figures 18 and 19 discloses only a few borderline situations, namely, GR-S black at 120° C, Butaprene-NXM gum at 90° and black at 100° C, Neoprene gum at 90° C, and black at both 90° and 110° C. Although the discrepancies never exceed a few thousandths of an inch in thickness, they serve to emphasize that these values are only approximations and that suitable margins should be allowed in choosing the thickness for oxidation and aging studies.

The variation of limiting sample thickness with temperature, as illustrated in Figures 18 and 19, for the black and gum stocks of each of the rubber types, is much more rapid for the GR-S stocks than for the others over the temperature range studied. The values for Butaprene-NXM and Neoprene stocks

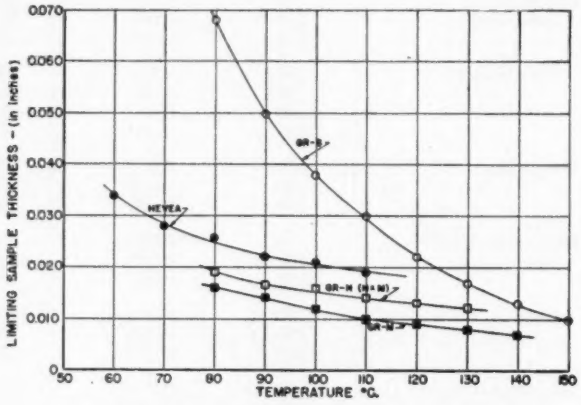

FIG. 19.—Limiting sample thickness of gum stocks *vs.* temperature.

change very slowly with temperature, whereas the Hevea stocks appear to be intermediate in this respect.

It should be pointed out that these values are the maximum thickness which permit oxygen to diffuse into the sample rapidly enough to support the chemical reaction at its maximum rate under the specific conditions of this test. At reduced oxygen pressure, for example, the rates of both reaction and diffusion would be changed and therefore the limiting value of the sample thickness would be altered. Safe limits of sample thickness must, therefore, be somewhat lower than these limiting values.

Finally, it should be emphasized that these limiting values concern the maximum rate attained in the final autocatalytic stage of the reaction. The properties of a stock are actually seriously degraded long before this stage of oxidation is reached, and for studies that do not extend into this region, a somewhat thicker sample may be employed.

LIMITING VALUES FOR CONSTANT-RATE STAGE

The limiting sample thickness values obtained from studies in the autocatalytic stage are generally much smaller than the 0.075 to 0.080 inch thickness

commonly employed for aging studies based on determination of changes in physical properties such as tensile strength. Aging tests are frequently confined to the earlier stages of oxidation, however, and thus may not involve the autocatalytic stage. The constant-rate period of oxidation is actually more important from a practical point of view, since the rubber is so badly degraded as to be useless by the time the autocatalytic stage is reached.

The presence or absence of limitation of the rate of oxygen absorption in the constant-rate stage by rate of diffusion is usually apparent on careful inspection of the oxygen-absorption curves for samples of different thicknesses. The accuracy with which the limiting value is bracketed depends on the original arbitrary selection of thicknesses to be studied. Safe limits of sample thickness for oxidation and aging studies which do not include the autocatalytic stage are pointed out in the following discussion and summarized in Table IV.

The oxygen absorption curves for the GR-S stock black as shown in Figures 4 and 5 of this paper and Figure 6 of a previous publication[2] indicate that the usual 0.075 to 0.080 inch thickness is satisfactory in the constant-rate stage up to a temperature of 110° C. A sample approximately 0.040 inch thick is satisfactory up to 130° C, but at 150° C the sample should not exceed 0.020 inch in thickness. The GR-S gum stock gives similar results based on the curves obtained at 110°, 120°, and 130° C, for example, see Figure 6. The sample of approximately 0.075 inch was satisfactory up to 120° C, but a thinner sample would be required at higher temperature.

The usual 0.075-inch thickness is satisfactory at 100° C for the natural-rubber black stock with added inhibitor, but this thickness results in limitation by diffusion at 80° C in uninhibited Hevea stocks. The oxygen absorption curves obtained at 100° C for the Hevea stocks are shown in Figures 8, 9, and 10. Similar data were obtained at the other temperatures listed in Table IV. A sample of 0.040 inch appears satisfactory for the gum stock at 80° C, for the uninhibited black stock up to 100° C, and for the inhibited black stock up to 110° C. For studies involving a natural rubber gum stock at 100° C, the sample should not exceed 0.020 inch in thickness.

Examination of the oxygen absorption curves for Butaprene-NXM, obtained at 90°, 100°, and 130° C (Figures 12 and 13) shows that thinner samples are required as compared to GR-S and natural rubber. A 0.040-inch sample is satisfactory in the constant-rate stage up to 90° C for gum stock and up to 100° C for black stock. At 130° C the samples should not exceed 0.010 to 0.015 inch in thickness if it is desired to avoid possible limitation by rate of diffusion.

The Neoprene data obtained at 90°, 100°, and 110° C (Figures 15 and 16) indicate values similar to those mentioned for the Butaprene-NXM stocks. Neoprene gum and black stocks in samples of approximately 0.040 inch thickness appear to be satisfactory up to 100° C. At 110° C, however, the sample thickness should be reduced to 0.020 to 0.025 inch to avoid limitation in the constant-rate stage by the rate of diffusion of oxygen into the sample.

The use of the data of Table IV for selection of sample thicknesses for a given aging or oxidation study requires the recognition that any deviations from the formulations, temperatures, and oxygen concentration used in this study may alter the situation somewhat. It must also be recognized that the values reported in Table IV are not limiting values but represent the thickest sample included in this study that was demonstrated to be free of limitation by diffusion. In many instances a somewhat thicker sample might be satisfactory, but considerable additional work would be necessary to locate the limiting values precisely.

Table IV shows that the amount of oxygen required to reach the start of the autocatalytic stage was approximately 15 to 25 cc. per gram (25° C and 760 mm.) for all stocks. Neoprene and Butaprene-NXM gum stocks tended toward the lower figure. An absorption of 15 cc. of oxygen per gram corresponds to approximately 2 per cent by weight which would, of course, result in a considerable deterioration of properties.

SUMMARY

Safe limits of sample thickness for rubber oxidation and aging studies, such that the chemical reaction rather than the rate of diffusion will be rate-controlling have been investigated for natural-rubber vulcanizates and for four synthetic-rubber types. For studies involving the entire range of oxidation, including the autocatalytic stage of rapid oxygen absorption, the conventional 0.075-inch thickness is frequently not satisfactory for accelerated aging and oxidation studies if it is desired to avoid limitation by diffusion. Only in the GR-S black stock was this thickness found to be satisfactory up to a temperature of 100° C. The other stocks, including natural rubber, Butaprene-NXM, and Neoprene black and gum stocks all require thinner samples to ensure that the observed rate of oxygen absorption is free of limitation by diffusion. A method of calculating the probable limiting value of sample thickness, above which the rate of oxidation in the autocatalytic stage is limited by diffusion, has been developed on the basis of volumetric oxygen absorption data obtained with GR-S. The method has also been applied to natural-rubber vulcanizates and to other synthetic-rubber types to locate the approximate limiting values at various temperatures for oxidation and aging studies which extend into the autocatalytic stage of rapid reaction.

The constant-rate period of oxidation is more important from a practical point of view than the autocatalytic stage, since properties are so seriously degraded as to make the rubber of little value before it reaches the final stage of rapid oxidation. Somewhat thicker samples may be used for studies that are confined to the earlier stages of oxidation. A 0.075-inch sample is free of limitation by diffusion in the constant-rate stage in the following cases: GR-S black and gum stocks at 110° C; Hevea black with added antioxidant at 100° C; and uninhibited Hevea black and gum stocks at 60° C. A 0.040-inch sample is satisfactory in this range for: uninhibited Hevea black at 100° and gum at 80° C; Butaprene-NXM black at 100° and gum at 90° C; and Neoprene black and gum stocks at 100° C.

ACKNOWLEDGMENT

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[2] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. **19**, 696 (1946).
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[4] Winn, Ph.D. thesis, Case Inst. of Technol., Cleveland, 1947.

WAX BLOOMING AND EXPOSURE CRACKING*

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GENERAL DISCUSSION OF EFFECTS OF NORMAL OUTDOOR AGENCIES ON VULCANIZED RUBBERS

There are a number of technical terms used to describe the types of deterioration caused by exposure to the normal atmospheric agencies, among which are exposure cracking, ozone cracking and sun checking or sun crazing. The agencies which cause these effects are usually considered to be (1) light, heat of the sun's radiation, and (2) ozone. These are normally all present at the same time and it is the type of article and the manner in which it is used that determines which of the two agencies causes the main types of deterioration. There are three physical conditions which affect the issue: (1) freedom from strain, (2) constant strain, and (3) periodic stress and relaxation, such as by flexing. The other controlling factor is the thickness of the rubber forming the product.

A summary of the normal effects is given in Table I.

Table I

Details of Deterioration Caused by Vulcanized Rubber by Normal Atmospheric Agencies

Conditions		Symptoms	Cause	Preventive measure
Unstrained	Thin	Serious stiffening	Light, heat, and oxygen	Antioxidant
	Thick	Surface crazing	Light and oxygen	Antioxidant
Strained (static)	Thin	Breaking	Ozone	Wax bloom
	Thick	Deep cracking	Ozone	Wax bloom
Flexed	Thin	Stiffening and cracking	Light, heat and oxygen	Antioxidant
	Thick	Cracking	Uncertain	Flex-cracking antioxidant

The part of the above table with which the present work is concerned is that dealing with strained rubbers; when exposed to the external atmosphere strained rubbers form small cracks at right angles to the direction of strain. This usually occurs within 48 hours of exposure, and the cracks go on deepening with time so that thin articles break quickly. This is due to traces of ozone in the atmosphere and goes on to just the same extent in complete darkness. Examples of this type of cracking are shown in Figures 1, 2, 3. Figure 1 gives an

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 27, No. 2, pages 103–126, April 1951.

example of the type of cracking which occurs on windscreen sealing strip; Figure 2 shows the two-directional cracks occurring on radiator hose due to the peripheral and longitudinal stretching; Figure 3 shows an example of complete failure of a rubber tube used on a milking machine; again the cracks are in two

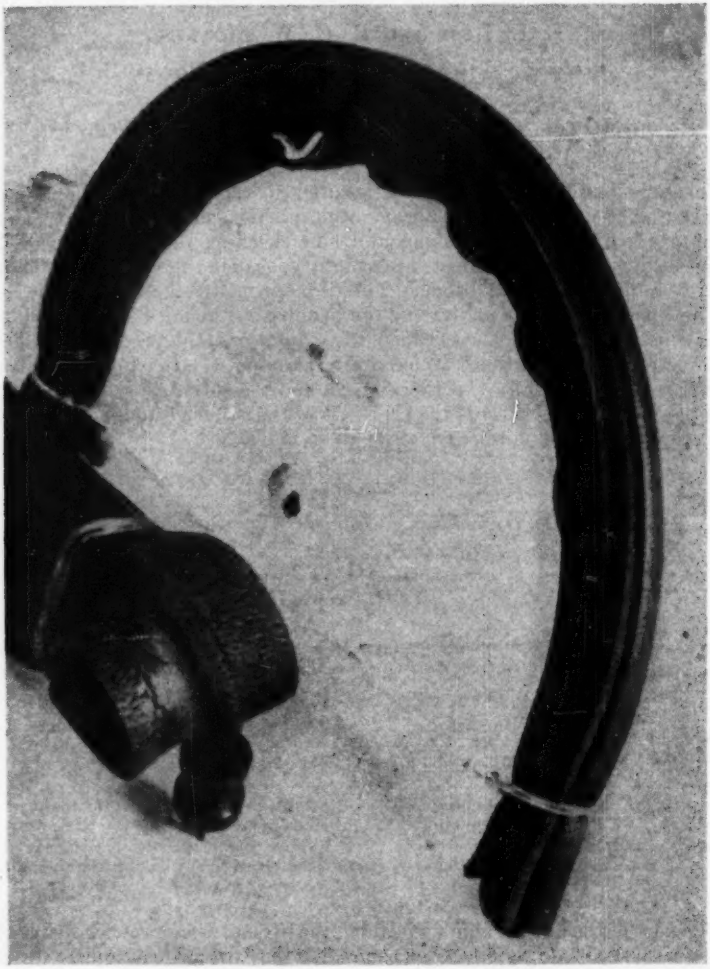

FIG. 1.—Ozone cracking produced in windscreen rubber sealing strip.

directions, in the middle due to bending of the whole tube and at the end due to stretching over a metal attachment. There is also an example of an antivibrational mounting which has cracked when under load and an example of suncrazing in a sheet of rubber exposed free from strain to sunlight.

In devising a compound for a product that may be exposed to the external

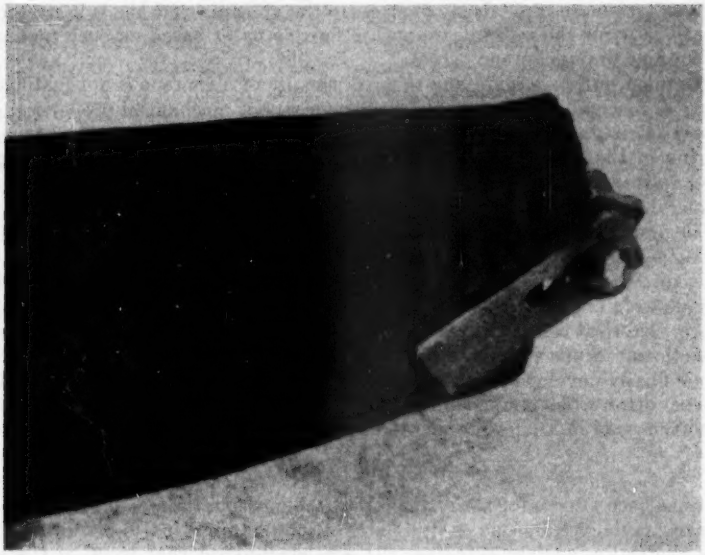

FIG. 2.—Cracks produced in service in a radiator hose.

atmosphere in a slightly strained condition, the courses open to the compounder are: (1) to base the compound on Neoprene or Thiokol, (2) to include in the compound, when based on natural rubber, a wax which will bloom out of the vulcanizate and thereby give a protective film on the surface, (3) to include in the compound, when based on natural rubber, large quantities of organic filler

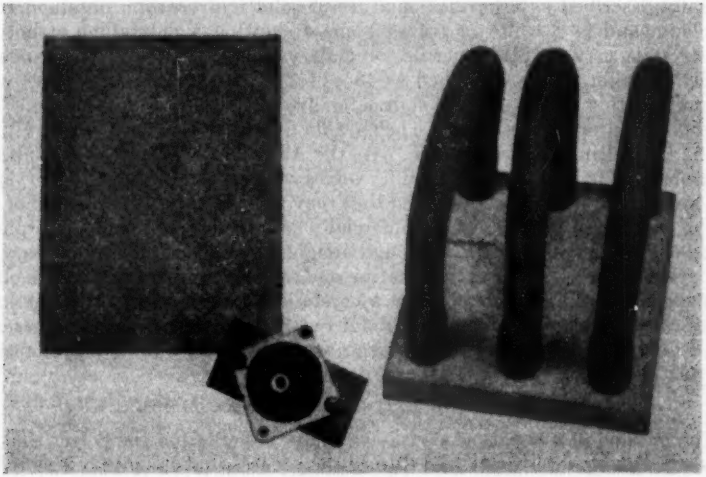

FIG. 3.—Two examples of ozone cracking and light or sun crazing on a sheet of rubber.

which will promote rapid decay of stress in the vulcanizate when it is stretched, and (4) to paint the vulcanizate with a flexible paint based on such materials as Neoprene or Vulcaprene.

For most purposes involving this risk the use of Neoprene is not justifiable; the use of method (3) gives rubbers with very poor mechanical properties, and method (4) is unsatisfactory because slight damage to the film or incomplete covering in the first instance results in worse cracking than with the unprotected rubber. For these reasons the wax protection method (2) was given considerable further study, and the results are described below.

The first requirement was to discover the conditions under which wax blooms develop and their rate of development. To do this, a method had to be evolved to measure the thickness of bloom on a piece of rubber. A number of possible methods were tried for this, including scraping off and weighing, optical interference, electrical resistivity, and direct measurement with a microscope, using cut-sections. Some success was attained with the last-mentioned method, but the one finally developed[1] consisted of swabbing the wax off a known area with plugs of cotton wool damped with petroleum ether and subsequently extracting the cotton wool in a micro extraction apparatus.

WAX BLOOMING

It has been known for many years that the incorporation of small quantities of waxes, usually from one to five parts on one hundred parts of rubber, provides protection against cracking. It was established that some of the wax migrated to the surface forming what was thought to be a protective film; it was also known that if flaws were produced in the film they were repaired by further blooming. Earlier work[2] on waxes and exposure cracking indicated the large variability between replicates with this method of protection, suggesting that further information was required on the process of wax migration.

The waxes that have hitherto been used for this purpose have always been petroleum waxes, either the material sold commercially as paraffin wax or those waxes sold under the trade names of Heliozone or Sunproof. Paraffin wax is normally described as a purified mixture of solid hydrocarbon obtained from petroleum and is a white or colorless mass showing a crystalline structure. The crystals may be plate, needle, or malcrystalline. The melting range of purified paraffin wax is described as 135–140° F. Other paraffin waxes with different melting ranges are sold commercially, and these contain the same wax and different proportions of oil. The paraffin wax used in the present investigation had a melting point of 122° F. As the American products Heliozone and Sunproof were both found to be mainly waxes with considerably smaller crystals than normal paraffin, it was assumed that they were essentially composed of the type of petroleum wax known commercially as microcrystalline or amorphous waxes. These waxes have a molecular weight averaging higher than paraffin wax, are derived from heavy lubricating and cylinder oil stocks, and are characterized, as their name implies, by a crystalline structure in which the individual crystals are on the average about one-fifth of those in normal paraffin wax. Commercial samples of this type were obtained, and were designated S72, S73 and S74.

DETECTION AND ESTIMATION OF WAX BLOOM

The method of estimation mentioned above suffers from the defect that, of necessity, the bloom is destroyed during the process, but in spite of this it has proved to be a most useful tool in this study.

Another inherent weakness of the method was failure to remove all the bloom from the test disc so that a wax detector was devised. This consists of a small electric heating element mounted on a glass holder such that when the holder touches the surface under examination the hot element is about 1 mm. from it. The surface immediately below the wire is then viewed with a reading lens from a low angle. As the wax melts it appears to recede from the point of heat application. The element is made of such a type of wire, and size that it gives a temperature of 80–90° C. This device is shown on the diagram in Figure 4. The microcrystalline waxes give films that produce normal optical

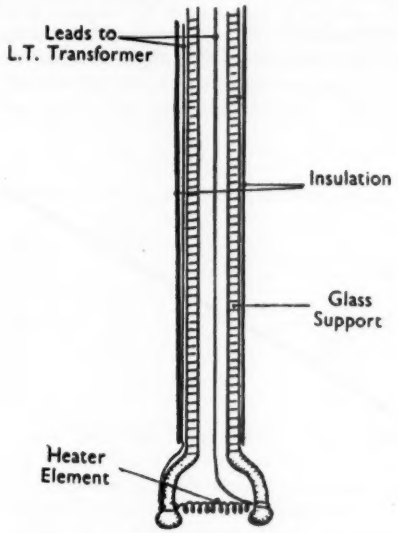

FIG. 4.—Spot heating device.

interference in the earlier stages of their growth; their color can be seen to change from green to yellow and then to red. But the film soon becomes too thick for this type of interference phenomenon. However, this does indicate the uniformity of the migration to the surface.

DEVELOPMENT OF WAX BLOOM FROM UNVULCANIZED RUBBER

Uncured stock was examined from various mixes. The stock was sheeted and cut into standard discs, and these were examined at intervals, the removal being effected by the method previously mentioned, except that in this case acetone-damped swabs were employed. Although the weight extracted is slightly larger than that from vulcanized rubber of the same composition, but without any added wax, probably due to other materials taken up by the swab, the wax film grows no thicker from 2 to 3000 hours after sheeting out. Therefore it seems that for some reason the wax does not migrate from the unvulcanized stock. It may be that it is solely the heat treatment during vulcanization that gives this migration effect, not necessarily the actual vulcanization process, or it may be that the solubility of the wax in unvulcanized stock is much greater

TABLE 2

DEVELOPMENT OF WAX BLOOM ON UNVULCANIZED RUBBERS

Time since compounding in hours	2	45	123	242	285	1387
Weight of extract in mg.	1.5	0.8	0.6	1.0	1.0	1.7

than in vulcanized rubber. Some typical results are shown in Table 2 for paraffin wax in a concentration of 5 parts in the base mix C, using 5 cm. diameter circular test-pieces. Similar results were also obtained using other waxes.

NORMAL DEVELOPMENT CURVE OF WAX BLOOM WITH TIME AFTER CURE

The process of migration to the surface is continuous, and thickness of bloom plotted against time after cure has a characteristic shaped curve which is

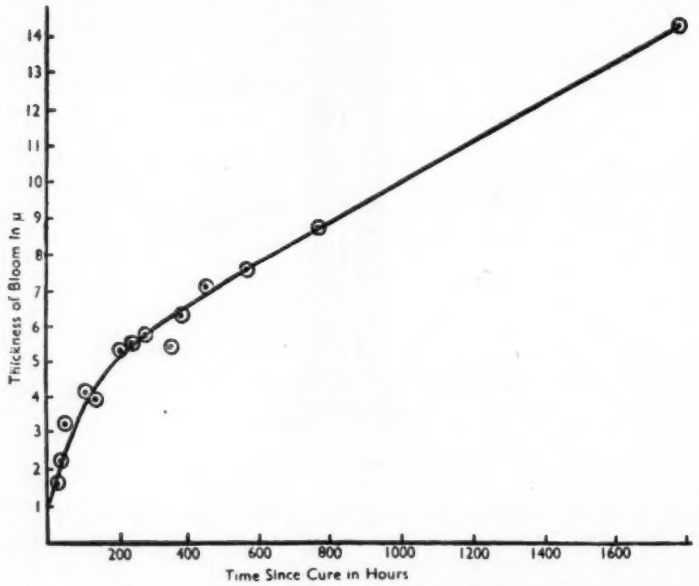

FIG. 5.—A typical development curve for paraffin wax bloom.

shown in Figure 5. Mix B, used for this particular development curve, is given below in Table 3.

TABLE 3

DETAILS OF MIXES

	Mix B	Mix C
Smoked sheet rubber	100	100
Zinc oxide	5	5
Stearic acid	2	2.5
M.P.C. black	5	50
Mercaptobenzothiazole	0.5	0.8
Paraffin wax	10.0	—
Sulfur	2.5	3.0

Vulcanized in the press for 15 minutes at 153° C.

The thickness of the wax film develops steadily with time after cure. The steep initial ascent of the curve, *i.e.*, where the surface bloom is being produced most rapidly, occurred in the first 10 days with this compound. It is obviously in this period that the blooming process is most efficient at repairing fractures in the bloom film. This curve was obtained by cutting a large number of discs from about $\frac{1}{16}$-inch thickness slabs of vulcanized rubber immediately after curing and removing the wax film from them one at a time at different periods after cure.

REGENERATION OF WAX BLOOM AFTER REMOVAL

When wax bloom is washed off the surface of a piece of vulcanized rubber, regeneration of the bloom appears to follow the normal growth curve from the point in time after cure when cleaning off ceases, as far as rate of growth is concerned. However, due to the effect of the solvent used in removing the initial bloom, the results can never be quite conclusive. The results are shown in Table 4.

TABLE 4

EFFECT OF REMOVAL OF WAX BLOOM AT INTERVALS AFTER CURE

Time for 1st bloom	Wt. of 1st bloom in mg.	Time for 2nd bloom in hrs.	Wt. of 2nd bloom in mg.	Total weight of wax removed in mg.	
21	4.2	284	2.0	6.2	
44	6.6	261	4.6	11.1	
116	8.4	189	4.9	13.3	Average = 11.7
140	7.9	165	2.6	10.5	
167	9.2	138	8.0	17.2	
188	9.6	117	1.7	11.3	

The initial bloom was removed from several discs at different times after cure, the cleaned discs were then all returned to a conditioning oven kept at 20° C after removal, and then all the films were removed together at some fixed time later; this is recorded in the table as the 2nd bloom. The total wax removed from each sample in the two extractions, as seen in the right-hand column, does not indicate any trend. If the bloom had been allowed to develop uninterrupted, the mass of wax migrating to the surface after 305 hours would have been 11.7 mg. This indicates that the regenerative property of the wax film is only a part of the normal development curve; the wax does not only grow where there are holes in the original bloom, but the film is thickening over its whole area.

EFFECT OF VARIOUS FACTORS ON THE RATE OF GROWTH OF WAX BLOOM

Effect of thickness of rubber on rate of growth of bloom.—The thickness of the rubber specimen does not appear to have a large effect on the diffusion of wax to the surface for the initial part of the development, but as the diffusion proceeds the rate of increase of thickness of bloom on the thicker samples tends to be considerably greater than on the thin samples. Some indication of this effect is given in Table 5, where the thickness of bloom developed on standard disc samples of different thicknesses is given. The results for the $\frac{1}{16}$-inch thickness samples give the approximate range of results obtained for the different cures.

Effect of wax concentration in the rubber on the rate of development of film.—The concentration was varied from one to ten parts of wax on a hundred parts

TABLE 5

VARIATION IN BLOOM THICKNESS WITH SAMPLE SIZE

Wax	Time since cure in hours	Thickness of bloom in microns for sample thickness (in.) 1/20	1/10	6/10
Paraffin	426	—	2 to 4	2.4
	2980	3.9	5 to 10	—
	4824	—	9 to 12	35.4
S72	426	—	0.5 to 1.5	1.4
	2980	0.5	2 to 4	—

of rubber. For paraffin wax with a melting point of 50° C, the family of curves for different concentrations, using base mix C, is given in Figure 6; the lower concentration is somewhat difficult to study, as the yield of wax is a little erratic. The effect of concentration is very much greater in the case of paraffin wax than with the other waxes examined. Varying the concentration with microcrystalline waxes S73 and S74 has little or no effect on the bloom development curve at room temperature, but the effect of concentration on the microcrystalline wax S72 can be seen quite clearly in Figure 6. In the same mix, five parts of this wax gives a similar curve to three parts of paraffin wax when stored at 20° C. However, this microcrystalline wax has two important advantages; the wax film when produced is very much stronger than that of the paraffin wax, and it has good adhesion to the rubber surface and in consequence does not tend to flake off if the film is thick. This wax bloom also produces a shiny pleasant appearance on the surface of the rubber.

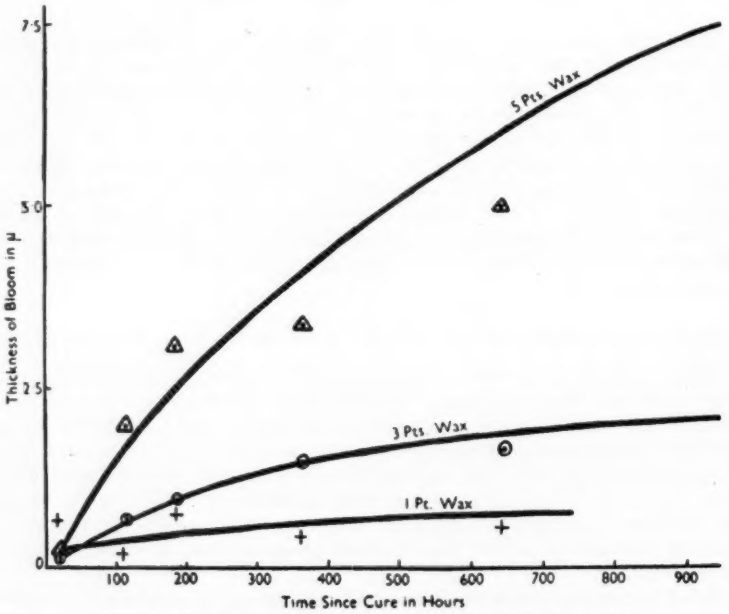

FIG. 6.—Effect of concentration on paraffin wax bloom development.

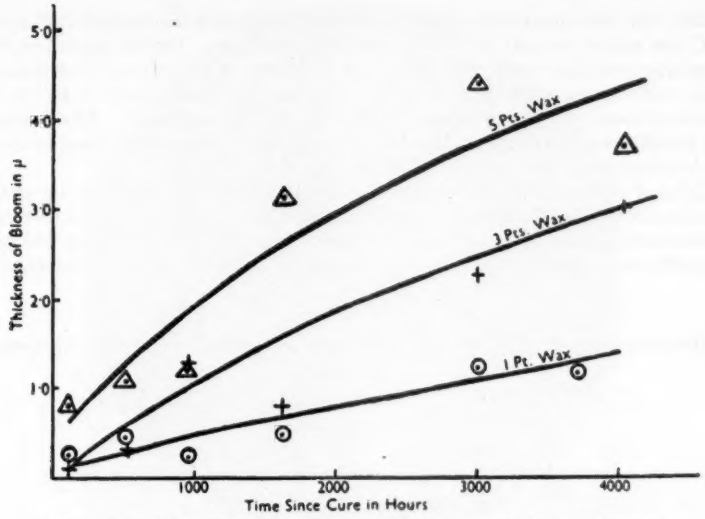

FIG. 7.—Effect of concentration of microcrystalline wax S72 on bloom development.

Effect of storage temperature on rate and growth of bloom.—The storage temperature has considerable effect, but this varies between one wax and another. This is probably due to the dual effect of temperature on the solubility of the wax in rubber and the rate of diffusion. The curves for representative waxes are shown in Figure 8. An interesting feature is the anomalous behavior of

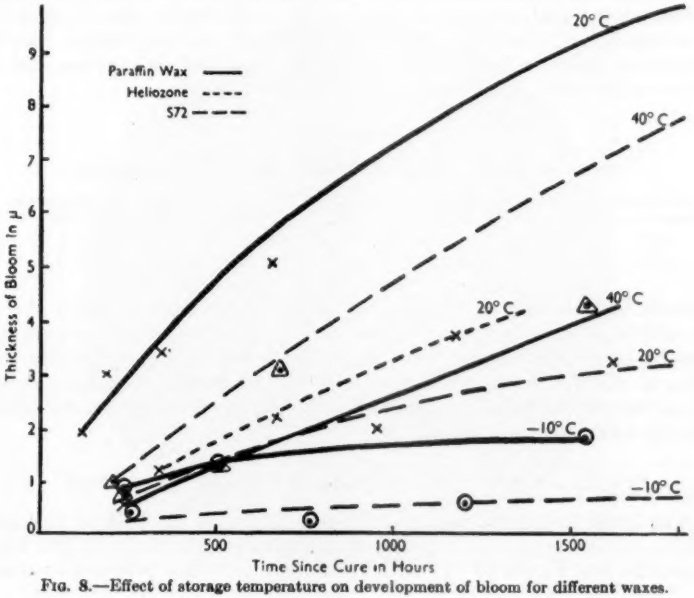

FIG. 8.—Effect of storage temperature on development of bloom for different waxes.

paraffin wax, the maximum migration of which occurs in the region of 20° and at 40° C the rate of formation of bloom on which drops. On the contrary, with the microcrystalline waxes S72, S73, and S74 there is an increase in amount of bloom with temperature up to 40° C. At temperatures about −10° C, the diffusion process slows down considerably in all cases examined. The tendency for a paraffin wax bloom to redissolve in the rubber when the ambient temperature is raised has been mentioned by Crabtree and Kemp[3].

Effect of stretching the rubber on rate of growth of bloom.—Rectangular shaped specimens stretched to 20 per cent elongation bloom at about the same rate as the unstretched specimens of equal surface area. The results using five parts of paraffin wax added to base mix C are given in Table 6. As these results were

TABLE 6

DEVELOPMENT OF WAX BLOOMS ON STRETCHED AND UNSTRETCHED RUBBER

Time since cure in hrs.	Thickness of wax bloom in microns: Unstretched	Stretched 20%
240	2.4	1.7
555	3.7	4.2
818	6.4	4.0
1051	7.6	6.5

produced from different batches tested at different times the effect of stretching does not appear to produce any difference in the yield of wax bloom as compared with the difference between replicate batches. Due to the ill-defined surface area being cleaned of wax bloom, the estimation is more inaccurate than that employed for unstretched rubber.

Effect of carbon black and inorganic fillers on rate of bloom.—The fillers used were whiting, magnesium carbonate, a medium thermal black, channel black, and china clay; equal volumes of filler on the rubber were used in mixes, details of which are given later. The thickness of microcrystalline wax film developed on vulcanizates of these mixes was measured, in microns, 333 and 645 hours after cure. The results are given in Table 7.

TABLE 7

EFFECT OF FILTERS ON THE DEVELOPMENT OF WAX BLOOM

Time since cure in hrs.	—	MPC black	MT black	Whiting	China Clay	Magnesium Carbonate
333	1.4	1.0	1.4	1.1	0.9	1.3
645	3.5	1.5	2.3	2.3	1.7	1.7

Generally there does not appear to be much difference between the wax bloom obtained using rubbers with the various fillers, but the pure-gum stock appears to give a significantly heavier bloom in the longer period after cure. Dilution of the wax due to the incorporation of filler implies that the amount of wax in the standard disc is reduced slightly, but this is insufficient to account for the large effect demonstrated.

PHYSICAL ASPECTS OF THE WAX IN AND ON THE RUBBER

It was found that there were wax crystals present in the bulk of vulcanized pure-gum rubber prepared from compounds containing added wax (see Figure 9 for paraffin and Figure 10 for microcrystalline), and their presence or absence

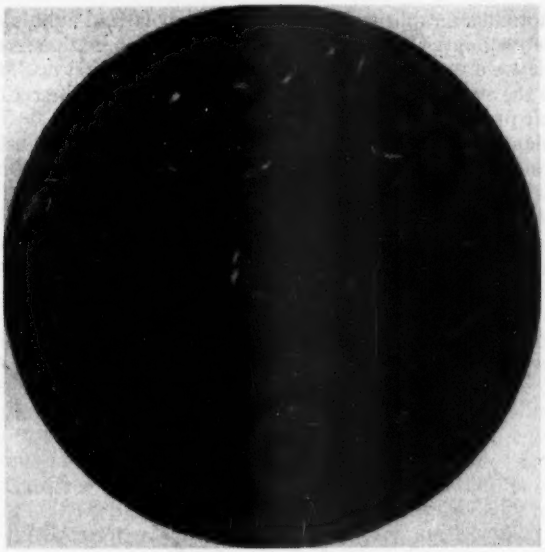

FIG. 9.—Paraffin wax crystals seen in vulcanized rubber. Magnification × 300.

could be used for an estimate of the solubility of wax in rubber. The concentration of wax on rubber was increased until a mix was found where a further increase in concentration caused the formation of wax crystals at room temperature which were visible in the rubber.

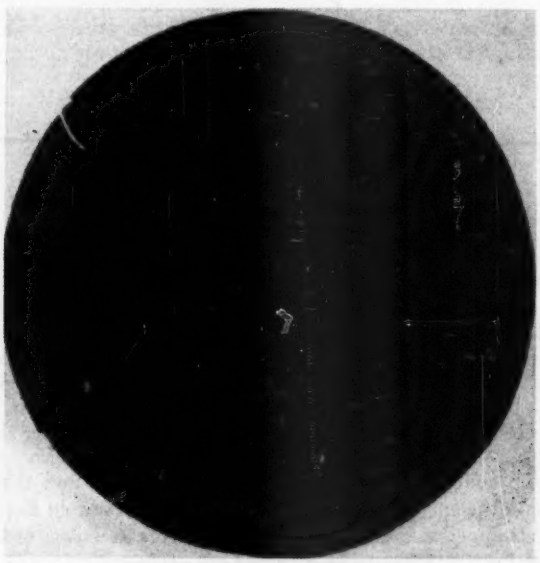

FIG. 10.—Microcrystalline wax crystals seen in vulcanized rubber. Magnification × 900.

These photomicrographs were obtained using polarized light, as the crystals are fortunately all optically anisotropic. Further examination has shown that these crystals are not visible in uncured stock. Generally it was found that no migration to the surface occurs until crystals are visible in the rubber, and presumably their presence indicates saturation.

An examination of the wax bloom itself on translucent mixes, using polarized light and a high power microscope, shows that the film is crystalline in nature and seems to have the same types of crystals as contained in films of the particular type of wax added to the compound.

Further examination of the wax film produced at the surface of the rubber indicates that the wax is not quite the same mixture of hydrocarbons that was

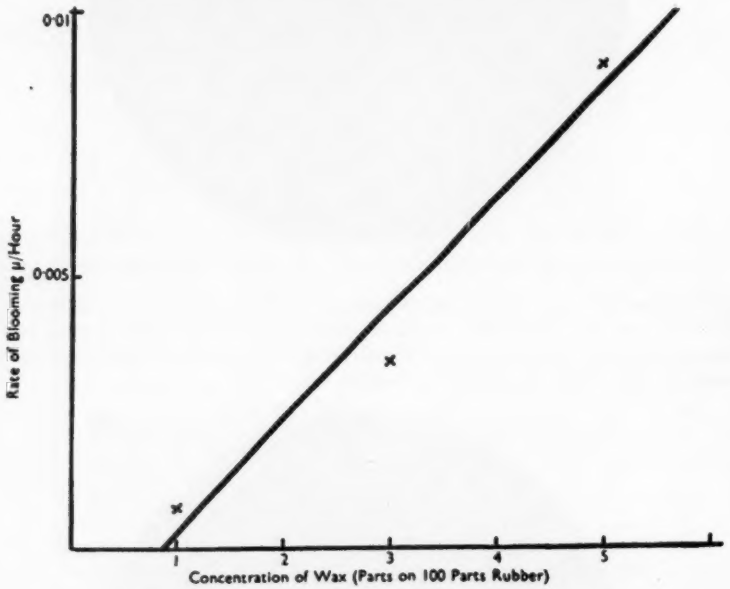

FIG. 11.—Influence of concentration on rate of migration.

originally incorporated in the mix. This was first suspected when it was found that the melting point of the recovered wax in the case of paraffin wax was 4° C higher than the original melting point, and for the microcrystalline wax, S72, 5° C lower than the original. This was followed up by an infrared spectroscopical examination of the waxes before and after diffusion through rubber. This analysis indicates that, with a pure-gum mix containing paraffin wax, there is a slight change representing a possible decrease in the unsaturated proportion of the wax, whereas with carbon black loaded rubber the same wax after diffusion is almost completely saturated. With the microcrystalline wax S72, the bloom contains some unsaturated components, and there is a very slight change in the spectrum which is probably a decrease in the unsaturated proportion. It appears, therefore, that carbon black accentuates the tendency for unsaturated components to be retained.

The solubility of wax in rubber was determined from the rate of diffusion at a fixed time after cure for various concentrations. This solubility figure, that is, the concentration where the rate of blooming is zero, was found to be about 0.8 part per 100 parts of rubber in the case of paraffin wax (see Figure 11) if one assumes a linear relationship at the lower concentrations.

This agrees well with the value obtained by the method using the disappearance of crystals in the vulcanized stock already mentioned. But no agreement was obtained between the solubilities determined by the two methods for the microcrystalline waxes, due possibly to the difficulty in detecting the earlier stages of development of these very small crystals.

If it is assumed that the rate of diffusion remains constant after about 1,000 hours (in fact it decreases gradually), then taking the above-mentioned figure for the solubility of paraffin wax, it is possible to calculate the minimum time the available wax in the rubber takes to migrate to the surface. For a standard disc, $\frac{1}{10}$ inch thick of a mix containing 10 parts of paraffin wax on 100 parts of rubber, the estimated minimum time for the wax to bloom is 542 days. It can, however, be shown that the rate of blooming is more nearly inversely proportional to the time after cure, in which case it seems more probable that the wax blooms for an infinite time. Nevertheless, from the point of view of protection against ozone and more especially regeneration of bloom after damage, the life is very much less. Wax bloom on rubber only migrates to a free surface. It was noticed that if a metal identification tag used in curing was left on the slab, no wax developed under it, but on removal the wax started to bloom.

OZONE CRACKING

TEST PROCEDURE FOR OZONE CRACKING EXPERIMENTS

The original R.A.B.R.M. technique with outdoor exposure used for testing rubbers for their resistance to ozone attack has already been described by Newton[4]. However, this method, although useful, gives rather variable results in the examination of rubbers incorporating waxes, due to the variable nature of

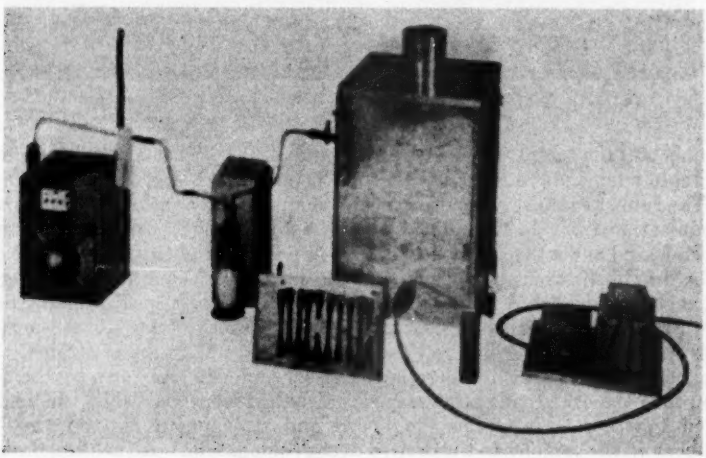

FIG. 12.—R.A.B.R.M. ozone test cabinet.

outdoor exposure conditions. A modified version of the Crabtree and Kemp[3] apparatus, illustrated in Figure 12, has been built so that approximately standard conditions of exposure can be maintained. The exposure cabinet depends on the generation of oxone from the oxygen of the atmosphere by an ultraviolet lamp which is fitted in the base of the cabinet in line with the plug shown on the front side. The rest of the apparatus shown consists of the power pack and the ancillary equipment used for measuring ozone concentration in the cabinet. The ozonized air is fed into a dark chamber by the convection stream caused by the heat from the lamp. This stream and, hence, the concentration can be varied by means of a damper fitted in the chimney. Throughout these experiments, the ozone concentration was kept at about 15 parts in 10^8 parts of air by

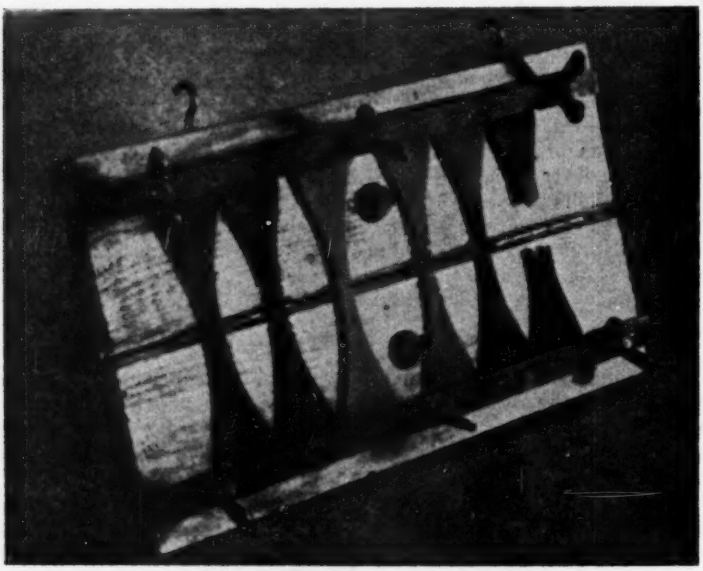

FIG. 13.—Folding board for mounting specimens.

volume, and the temperature between 26 and 32° C. This latter variation unfortunately depends to a large extent on the ambient temperature.

The rubber samples are cut by means of a press die as soon as possible after vulcanization from $\frac{1}{10}$-inch thick slabs of molded rubber, care being taken at this stage to handle the specimens as little as possible and only then by the ends of the dumbbell, which are of uniform width. The old method of nailing the specimens on to a board while stretched was replaced by a special folding board shown in Figure 13, which obviates the necessity for holding down the specimens while nailing and gives all the samples the same range of strains. The specimens are first placed under one metal bar and clamped down by the wing-nuts; then the other ends are fastened under the second bar while the board is folded together. Flattening the board and fastening a clip on the back stretches all the samples to the desired overall elongation. An arbitrary system of crack grading has been adopted, using the figures 1 to 10. The grading de-

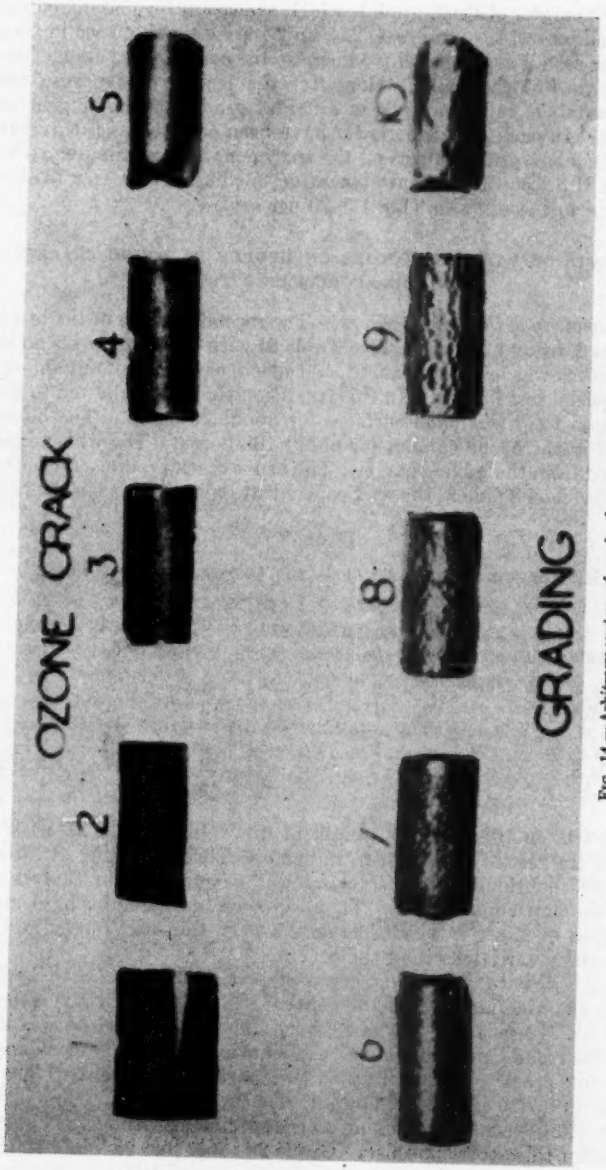

FIG. 14.—Arbitrary system of grades for ozone cracking.

pends on the size and number of cracks, ranging from grade 1, which are only visible with a pocket lens, to 10, when the rubber sample is cracked completely through. Examples of these grades, which are useful for making comparisons are given in Figure 14. Grades 1, 2, 3 and 4 are difficult to see in the photograph, as the cracks are so small (to increase the contrast the cracks have been whitened with French chalk). Hereafter the results of exposure tests will appear as numbers representing the different grades of cracking in specified strain areas. In each case the grades have been assessed as the average over each of three initial strain ranges on the specimen; high strain area (referred to hereafter as H.S.) 35–50 per cent elongation, medium strain area (M.S.) 20–35 per cent, and low strain area (L.S.) 5–20 per cent.

EFFECTS OF VARIOUS FACTORS ON DEGREE OF OZONE CRACKING IN THE ACCELERATED TEST

Reproducibility of the test procedure.—The reproducibility of the test method was examined, using base mix C (see Table 3) with different waxes added to it. A batch of stock was mixed and cured, and specimens were cut out and stretched on to the special test boards. In this condition they were allowed to develop a wax bloom on their stretched surfaces for about 20 hours. The boards were then placed in the ozone cabinet for about 100 hours. The whole experiment was repeated from the mixing stage. The ozone crack gradings for both experiments are given on Table 8; the wax concentration is given, as in the rest of this

TABLE 8

REPRODUCIBILITY OF ACCELERATED OZONE EXPOSURE TESTS

Mix		C	C1	C2	C3	C4	C5	
Wax		None	Paraffin	S72	S73	S74	S72	
Concentration of wax		—	5	5	5	5	1	
Ozone	H.S.	2	2	—*	3+	5	2	1st Test
	M.S.	2	1	—*	2	1	3	
	L.S.	—	—	—	—	—	1	
Crack grading	H.S.	2	2	—*	3	2	2+	Replicate
	M.S.	2	2	—*	2	1	2	
	L.S.	—	—	—	—	—	1	

paper, in parts on 100 parts by weight of raw rubber. The asterisk* is used throughout the rest of the paper to indicate localized cracking at the edges or where it was considered that cracking was so nonuniform that it was not typical of the particular rubber. The results are in reasonable agreement with the exception of mix C4, which has only a very thin wax bloom and is more liable to chance variations than the others.

Effect of different waxes on the degree of protection against ozone.—The base mix C was again employed and the concentration of the various waxes varied between 1 and 10 parts on 100 of rubber. The test procedure was described earlier. The results, after 100 hours' exposure are given in Table 9, and are the average ozone crack gradings of up to 10 separate experiments. The rubbers containing wax were allowed 20 hours to develop any bloom before exposure to ozone. It will be seen that cracking on the specimens without wax bloom is not very bad after this short exposure. Grade 2 is only just visible with the naked eye, the cracks being small and very shallow, while grade 1 is visible only with a pocket lens.

TABLE 9

OZONE PROTECTION CONFERRED BY DIFFERENT WAXES

Wax	Concentration (parts on 100 of smoked sheet)	Ozone crack grading		
		H.S.	M.S.	L.S.
None	—	2	2	1
Paraffin	5	2	2	<1
S72	1	2+	2+	1
	5	—*	—*	—
	10	—	—	—
S73	5	3	2	—
	10	—	—	—
S74	5	3	1	—
	10	1	—	—
Heliozone	5	1	—*	—
	10	—	—	—

With paraffin wax, the grading throughout is much the same as with the unprotected rubber, but with S72 at the lowest concentration the cracking is slightly worse than with the unprotected rubber, as it is also with the lower concentrations of S73 and S74. Larger proportions of wax S72, however, give good protection, as also does Heliozone.

Generally, therefore, it appears that the microcrystalline waxes S72 and Heliozone give better protection than paraffin wax at an equal concentration in rubber under these conditions of exposure. The majority of waxes, however, give some degree of protection in the lower strain ranges, that is at 5–35 per cent elongation, but in the higher strains it is apparent that the incorporation of insufficient or an ineffective wax may increase the cracking beyond that which would be experienced with the unprotected rubber. This is probably due to the attack being restricted to the limited areas exposed by flaws or brakes in the wax film, thus producing a small number of large deep cracks instead of the multiple small ones produced on the wax-free mix. It is interesting to note that paraffin wax, which is widely used, does not appear to give any protection under these conditions of exposure in spite of the very much thicker bloom which develops, and that it behaves very much as if there were no continuous film over the rubber surface. The failure of paraffin wax in this respect may well be explained by the large size of the paraffin wax crystals, which cannot pack tightly enough to give an impervious bloom, and the poor adhesion between the rubber surface and the paraffin wax bloom, although it is of interest to note that under outdoor conditions of exposure during the winter paraffin wax was found to give a considerable degree of protection against atmospheric ozone. This failure of paraffin wax under accelerated ozone cracking conditions has already been noticed by several authors including van Rossem and Talen[4].

Effect of thickness of wax bloom on degree of protection.—The main difference introduced by varying concentrations of waxes, and also by varying samples within a given type of wax, *e.g.*, microcrystalline type, appears to be the difference in thickness of the blooms developed. Using the data obtained on the migration of wax to the surface, it has been possible to make an estimate of the thickness of the bloom when the sample is exposed and to estimate the minimum thickness of wax film required to give protection. The data given in Table 10 represent the thickness of films of wax S72 on a tire-tread type mix at the commencement of exposure, the varying thicknesses being produced by altering the

TABLE 10

THICKNESS OF MICROCRYSTALLINE WAX BLOOM TO GIVE ADEQUATE OZONE RESISTANCE

Thickness of wax film in microns	Ozone crack grading: H.S.	M.S.	L.S.
0.07	2	3	1
0.10	3	2	—
0.10	1	<1	—
0.15	—*	—*	—
0.50	—*	—	—
0.70	—*	—	—
1.10	—	—	—
1.70	—	—	—

time of storage before exposure, the storage temperature, or the wax concentration.

It therefore seems that, when the thickness of film is about 0.15 microns, it gives protection against an exposure of in excess of 100 hours under the conditions in the ozone cabinet over all ranges of strain examined. This is about 6 millionths of an inch, so only a very thin film of this wax is needed to give protection against ozone of the concentration ever likely to be experienced in the normal external atmosphere at ground level.

With parafin wax the film thickness was varied from 0.4 to 3.2 microns, and the results of the cracking are almost the same throughout, which implies that the film thickness as far as paraffin wax is concerned is not so relevant.

Effect of carbon black and inorganic fillers on the degree of protection afforded by microcrystalline wax.—In this series of experiments the effect of introducing equal volumes of various fillers in the base compound was examined.

Using a base mix consisting of smoked sheet 100, zinc oxide 5, stearic acid 1, mercaptobenzothiazole 0.8, and sulfur 2.5, a range of compounds were prepared and vulcanized containing MPC and MT blacks, whiting, china clay, and magnesium carbonate, both with and without five parts of microcrystalline wax.

The effect of fillers in the mix on the growth of bloom as has already been stated and is not very marked except that the pure-gum stock gives a thicker bloom than those mixes with fillers. The conditioning of the test-pieces, *i.e.*, 20 hours to develop bloom in the stretched condition, before exposure to ozone and 100 hours in the cabinet were used as described earlier. The results of the tests are given in the following table.

The cracking of the unprotected rubbers, although not severe, except in the case of the specimen using M.P.C. black as a reinforcing agent, was entirely

TABLE 11

EFFECT OF FILLERS ON THE RESISTANCE TO OZONE ATTACK OF VULCANIZED RUBBER WITH AND WITHOUT WAX BLOOM

Filler	Ozone crack grading: With 5 parts S72 H.S.	M.S.	L.S.	Without wax H.S.	M.S.	L.S.
None	—	—	—	2	2+	2
M.P.C. black	1	—	—	2+	5	1
M.T. black	—	—	—	3	3	2+
Whiting	2	—	—	3	2	2
China clay	1	—	—	3	2+	2
Magnesium carbonate	—	—	—	3	2	2

eliminated in the medium and low strain areas by the incorporation of the wax S72, and was reduced in the high strain areas. The mixes with clay and whiting fillers appear to be particularly susceptible to ozone cracking, as already reported by Newton[4], and the wax does not give adequate protection in the high strain area. If instead of allowing the wax to bloom for about 24 hours on the stretched samples, they were stored for some time and then stretched, more severe cracking occurred in the high strain area.

TABLE 12

EFFECT OF SOFTENERS ON THE PROTECTIVE ACTION OF WAXES

Wax	Strain area	Softener: None	Pine tar	Mineral oil	Medicinal paraffin	Petroleum extract	Dibutyl phthalate
Paraffin	H.S.	1	1	2	3	2	1
	M.S.	1	—	2+	3	1	1
	L.S.	—	—	1	—	—	1
S72	H.S.	—	—	—*	—*	—	—*
	M.S.	—	—	—*	—*	—	—
	L.S.	—	—	—	—	—	—

Effect of various softeners in the mix on the protection afforded by microcrystalline wax.—A range of compounds were prepared from a base mixture of smoked sheet 100, zinc oxide 5, stearic acid 2.5, mercaptobenzothiazole 0.8, sulfur 3, and M.P.C. black 50, with additions of 7.5 parts of pine tar, mineral oil, medicinal paraffin, petroleum extract, and dibutyl phthalate. In addition, to one series 5 parts of paraffin wax was added and to another 5 parts of S72 microcrystalline wax. These were all vulcanized, and the usual test specimens

TABLE 13

MIX DETAILS

Smoked sheet	←100→			
Neoprene-GN		←100→		
Hycar OR-15			←100→	
Perbunan				←100→
Zinc oxide	← 5 →	← 1 →	← 5 →	← 5 →
Stearic acid	←2.5→		←0.5→	←0.5→
Light calcined magnesia		← 4 →		
Pine tar	←4.5→			
M.P.C. black	← 50→			
S.R.F. black		← 50→	← 50→	← 50→
Mercaptobenzothiazole	←0.8→			
Benzothiazyl disulfide			←1.5→	←1.5→
Sulfur	← 3→		←1.5→	←1.5→
Paraffin wax	— 5 — —	— 5 — —	— 5 — —	— 5 — —
Heliozone	— — 5 —	— — 5 —	— — 5 —	— — 5 —
S72	— — — 5	— — — 5	— — — 5	— — — 5

prepared. Two sets of these specimens were stretched and allowed to develop a wax film for 71 hours. The paraffin wax was affected by the various softeners. In some cases it seems to have almost entirely prevented the migration of the wax to the surface. On the other hand, wax S72 seems to be very little affected by the softeners and gives its normal resistance to ozone attack. The full results are given in Table 12.

TABLE 14

EFFECT OF VARIOUS WAXES ON THE OZONE RESISTANCE OF SEVERAL TYPES OF RUBBER

Wax	Rubber: Natural	Neoprene-GN	Hycar OR-15	Perbunan
Paraffin	3	—	2	1
	1	—	1	—
	—	—	—	—
Heliozone	1	—	—	—
	—	—	1	—
	—	—	—	—
S72	—*	—	4	5
	—	—	—	3
	—	—	—	—
None	2	—	2	3+
	2+	—	3	3
	1	—	3+	4

Effect of ozone exposure on compounds from various synthetic rubbers.—The rate of blooming of wax from Hycar and Perbunan is about half that obtained with natural rubber, and the results of ozone exposure on the Perbunan and Hycar samples with or without waxes is quite marked, as seen by the results given in Table 14. The uppermost figure in each division indicates the ozone crack grade in the high strain area and the lowest the grading in the low strain area. Neoprene did not crack with or without wax protection. The details of the actual mixes used are given in Table 13, conditioning of test-specimens and exposure were as described earlier.

Wax S72 gives much better protection on Hycar and Perbunan if given longer periods, *e.g.*, four or five days, either stretched or unstretched before exposure, to develop a protective film. This is to be expected in view of the slow bloom development on these rubbers.

Effect of slight flexing at intervals during exposure to ozone.—In all the work so far described all the waxes were allowed to migrate and give their protection, if any, under as far as possible the optimum conditions. A more severe semi-dynamic test was given to a group of samples prepared from a tire-tread type of mix, with 10 parts of wax on 100 parts of rubber. The specimens were taken out of the cabinet during the exposure and flexed several times by folding the board in half; this was repeated five times during the exposure. The crack gradings are given in Table 15 after 169 hours' exposure for the flexed specimens and 144 hours for the normal exposure test.

A considerable degree of resistance against ozone attack was given by the microcrystalline waxes, even under the moderate physical disturbance caused by stretching and relaxing the specimen several times.

TABLE 15

COMPARISON OF NORMAL AND FLEXED EXPOSURES USING HIGH CONCENTRATIONS OF WAX IN THE RUBBER

Wax	Normal exposure: H.S.	M.S.	L.S.	Flexing exposure: H.S.	M.S.	L.S.
S72	—	—	—	1	—	—
S73	—	—	—	1	2	—
S74[1]	1	—	—	8+	—	—
Heliozone	—	—	—	<1	—	—

DISCUSSION OF THE PRECAUTIONS NECESSARY IN USING WAX BLOOMS FOR PROTECTION AGAINST OZONE CRACKING

The main points that arise out of this work are as follows.

In general, each wax must be capable of migration through the rubber, for some waxes do not bloom sufficiently, even after comparatively long periods, to give protection against ozone attack. A sufficient quantity must be incorporated in the mix to give the necessary film thickness soon after cure. In the case of the microcrystalline waxes this seems to be about five parts on 100 parts of natural rubber. A lesser quantity of wax is required if a relatively high rubber content stock is used, *e.g.*, three parts on 100. Where possible, waxes with very small crystals should be employed because of their ability to pack tighter in the wax bloom and to give better physical properties to the wax films; for example, paraffin wax with large crystals has a low elongation at break and its film has poor adhesion to the rubber surface. The use of wax protection should be restricted to strains of not more than 30 per cent elongation. Although in some cases it has been found possible to protect rubbers at about 50 per cent elongation, it is generally safer to keep to the lower strain ranges. If possible the article should be mounted or stretched immediately after cure and stored indoors to enable the wax bloom to develop on the stretched rubber in a low ozone concentration. If it is required to protect Hycar or Perbunan rubbers with waxes, the bloom should either be given a longer period to grow or, alternatively, a larger proportion of wax should be incorporated in the mix. The removal of these films by accident is fairly easy, even with the microcrystalline waxes, which give very much better adhesion than ordinary paraffin wax. So it is necessary to educate the user and prevent him polishing off the dull bloom or otherwise cleaning the exposed surfaces. The rubber product should be removed as soon as possible from the mold after vulcanization to allow the wax free surfaces to which migration can take place. Paraffin wax migration, although more rapid than any other wax examined at normal temperature, appears to be more sensitive to the presence of other softeners, time of cure, and temperature, than the microcrystalline waxes, although these latter waxes are more affected by a change of rubber. All these factors must be taken into account when designing the mix for each specific task.

It does seem essential that any manufacturer employing this method of protection against ozone cracking should make sure by suitable tests that, in the mix used, the conditions are such that an adequate bloom will develop sufficiently quickly and be allowed to remain relatively undisturbed during the required service. Unless this is done, this work suggests that very much worse cracking may easily result than if no wax at all is used in the mix.

SUMMARY

A brief résumé is given of the types of deterioration which cause cracking and similar forms of deterioration in vulcanized rubber and the possible remedies.

A study has been made of the development of wax bloom on rubber and some of the factors which affect this development. The waxes constituting the blooms have been examined, as has the wax in the bulk of the rubber.

The protection afforded by these wax blooms against ozone attack on various base mixes with both natural and synthetic rubber has been determined, using a standard technique for the ozone exposure.

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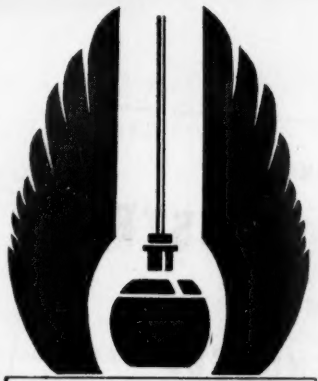

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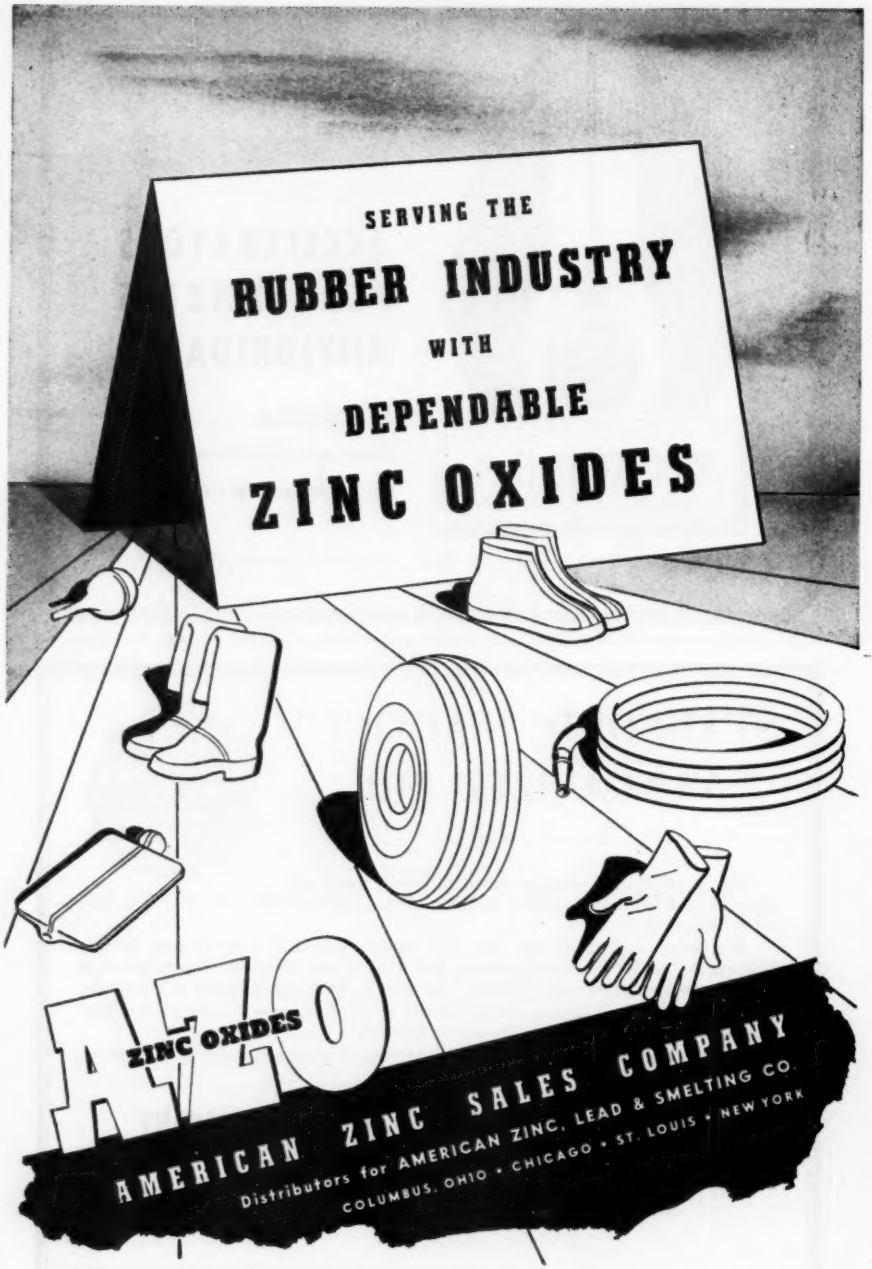
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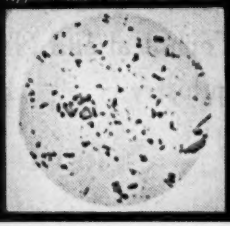

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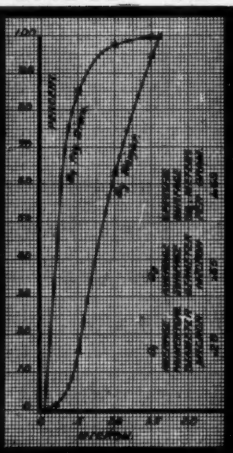

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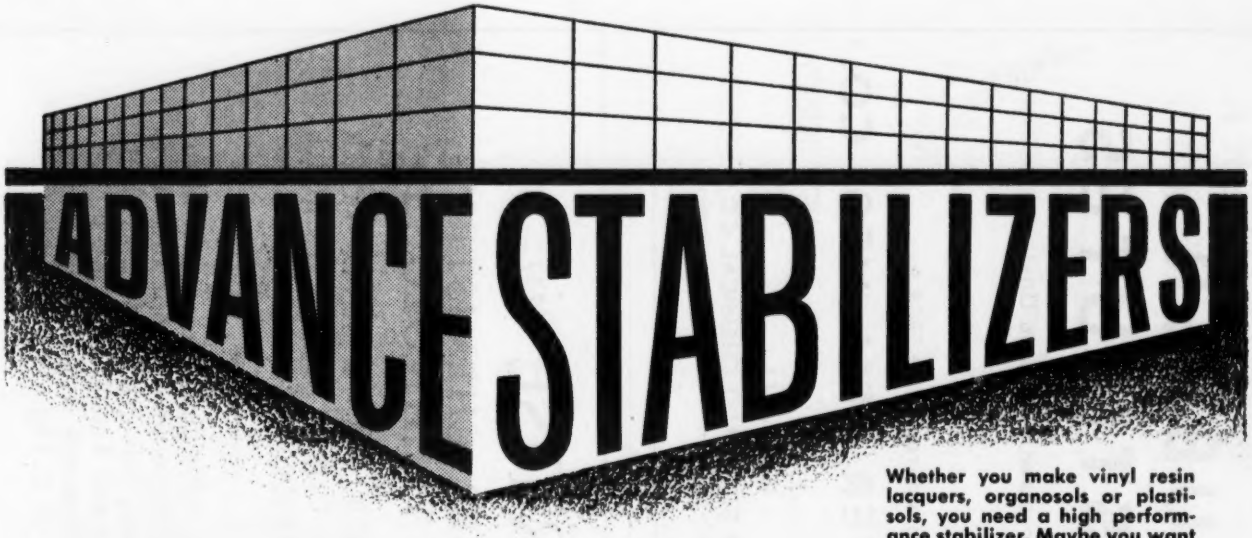

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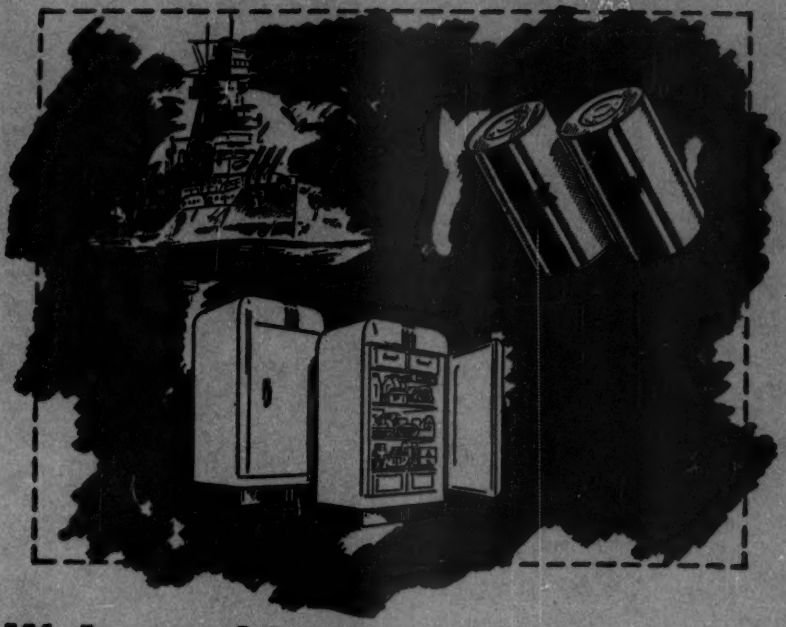

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